



**Tatiana Mendes Ferreira Vitorino**

Mestre em Conservação e Restauro

## **A closer look at nineteenth century cochineal lake pigments through historical recipes reconstructions**

Dissertação para obtenção do Grau de Doutor em  
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Especialidade em Ciências da Conservação

Orientador: Doutor Marcello Picollo, Investigador, “Nello Carrara” Institute of Applied Physics, National Research Council, Italy

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FACULDADE DE  
CIÊNCIAS E TECNOLOGIA  
UNIVERSIDADE NOVA DE LISBOA

**Maio 2020**





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*Ao Avô Zé e àqueles a quem mostrou o que é o Amor.  
Aqueles a quem tenho a sorte de chamar Família.  
E, sempre com lugar de destaque, à Mãe e ao Pai.*



# Agradecimento

Isaac Newton - diz-se - tornou conhecida a metáfora “If I have seen further, it is by standing upon the shoulders of giants.”.

A conclusão deste doutoramento deve-se a um raciocínio semelhante, ainda que com um significado diferente. Se está concluído, foi porque fui amparada por gigantes. Uns, gigantes, não em termos de dimensão física, mas ao nível do apoio que dão, da motivação que proporcionam, da força e do tempo que partilham, da confiança e segurança que transmitem, da proteção e cuidado grátis, da paciência e bondade infinitas, da capacidade de compreensão e de aceitação, da amizade sem limites, do acreditar constante, do amor sem explicação. Outros, gigantes, em termos profissionais e académicos, com mentes brilhantes, perspetivas inteligentes, cheios de conhecimento e experiência. Uns mais gigantes do que outros, uns mais constantes do que outros, mas tendo em conta que estou grata a todos, este agradecimento é geral. As palavras, essas, serão sempre muito poucas e gastas para se agradecer tanto, e o espaço e tempo para escrever são curtos, mas fica a tentativa.

Um gigante estrangeiro, Marcello Picollo, que aceitou percorrer este caminho sem saber bem o que lhe ia calhar, mas que nunca desistiu de ser gigante. Foi um caminho de conquista de confiança da Ms Go, no entanto, ainda hoje, tenho dificuldade em perceber a razão pela qual acreditou constantemente em mim. A sua presença foi mais importante do que alguma vez lhe conseguirei mostrar. Felizmente, este gigante andou muitas vezes acompanhado por outros três gigantes, Costanza Cucci, Andrea Casini e Lorenzo Stefani, sempre extraordinários a dedicar-me tempo quando não o tinham. Um gigante, Vanessa Otero, que foi sempre o meu maior exemplo e, num caminho onde o trabalho se entrelaçou com a amizade, é a razão de ser de tudo o que esta tese tem de bem feito. Um gigante, Professor Jorge Parola, que ajudou a relativizar o que por vezes, e injustamente, parecia ser o fim do mundo. A estes três gigantes orientadores, agradeço do fundo do coração pela oportunidade, no geral, e por todas as oportunidades, em particular, após os erros, medos, dúvidas, inseguranças, desilusões e, mesmo, alguma apatia. Em tantos momentos, caracterizados por estes sentimentos, não celebrei o trabalho desenvolvido. No entanto, foi sempre um orgulho enorme ter-vos como orientadores. Fui uma privilegiada.

Gigantes que, no todo, dão pelo nome de Família, e, no particular, são conhecidos como a Mãe, o Pai, o Diogo, o Tiago, a Avó Lina, a Mariana, a Filipa, a Isabel, a Tia Ana, o Mário e o Sérgio. E um gigante tão tão grande e especial que não cabia mais na Terra e acabou por ir para o Céu, que dá pelo nome de Avô Zé. *Avô, não é o tipo de doutora que pensavas, mas sempre terás uma neta doutora.*

Um outro gigante, Tiago, que surgiu neste caminho difícil e que - tudo indica - veio para ficar, fazendo crer que, só por isso, o percurso valeu a pena. Felizmente, este não veio sozinho e trouxe

com ele a Isa, o António e o Ricardo.

Gigantes que, no todo, dão pelo nome de Amigas, e, no particular, são o meu Diagrama de Venn, Andreia Mendes e Raquel Marques, a minha Number 1, Catarina Geraldês, as minhas amigas de coração, Joana Devesa e Francisca Lourenço, e as minhas babes, Daniela Pinto e a Magda Viana. Outros, que começaram por ser colegas e acabaram por ser os gigantes Inês Soares, Márcia Vieira, Paula Nabais, Artur Neves e Rita Araújo. E, ainda, aqueles que tornaram Florença numa segunda casa, Paola Di Ninni, Letizia Di Bartolo, Filippo Cherubini, Filippo Micheletti, Italo Celiento, Alessio Dezi, Marco De Vita e Francesca Martemucci.

Outros, cujas palavras, atitudes ou tempo disponibilizado, momentâneos ou esporádicos, também ampararam: Ana Maria, Isabel Pombo Cardoso, Professora Leslie Carlyle, Professora Joana Lia, Professora Maria João Melo, Julio del Hoyo-Meléndez, Antoine Stopin, Cristina Montagner, Élia Roldão, Juliana Buse, Giovanni Bartolozzi, Marilena Ricci, Maurizio Becucci e Professor Victor de Freitas. Também, as meninas do DCR e o pessoal do Laboratório de Fotoquímica; os alunos e colegas que, por momentos, se tornaram bem mais do que isso; os colegas do projeto COSCH; e todas as pessoas que possivelmente se cruzaram com este caminho e o tornaram mais completo, mais feliz ou menos cansativo, cujos nomes ficam em falta, porque o percurso foi longo e a memória vai dando de si.

A todos os gigantes, mais do que a certeza de que ampararam um doutoramento, fica a certeza de que ampararam o crescimento, a aprendizagem, o desenvolvimento e o fortalecimento desta pessoa, quer em termos profissionais e académicos, quer em termos pessoais. Um dia, ouvi alguém dizer, sobre doutoramentos, que qualquer semelhança entre a tese final, o projeto inicial e os planos traçados é pura coincidência. A ser verdade, esta tese não foi exceção. Muito ficou por investigar, descobrir e criar. De uma questão que se colocou, duas nasceram e três ficaram por responder. No entanto, hoje sou mais completa, mais corajosa, mais resiliente e - talvez - um pouco menos ignorante. A tese, essa, é a prova de tudo isso. Está pronta a ser refeita e, se a pudesse fazer de novo, faria de forma diferente. Faria gigantescamente melhor.

Por fim, agradeço ao DCR/FCT-UNL e ao IFAC-CNR, e às pessoas que fazem estas instituições, e agradeço à Fundação para a Ciência e Tecnologia e ao Programa Doutoral CORES (PD/00253/2012), pela bolsa de doutoramento PD/BD/105902/2014 que me permitiu subir este degrau de onde, sentindo-me sortuda, olho com orgulho e admiração para todos os gigantes.

# Acknowledgment

It is said that Isaac Newton made famous the metaphor “If I have seen further, it is by standing upon the shoulders of giants.”.

This PhD is now concluded thanks to a similar thought, with a different meaning though. If it is concluded, it is because I stood on the shoulders of giants. Some, giants, not with respect to their size but with respect to the support they provide, the motivation they give, the strength and time they share, the confidence and safety they transmit, the free protection and care, the endless patience and kindness, the ability to understand and to accept, the friendship without limits, the constant believing, the love without explanation. Others, giants, professionally and academically speaking, with bright minds, smart perspectives, full of knowledge and experience. Some more giants than others, some more constant than others, however, considering that I am grateful to all of them, this acknowledgment is general. Words, those, will always be too scarce and worn-out to acknowledge so much, and the space and time to write are short, but here is my attempt.

A foreign giant, Marcello Picollo, who accepted to walk this path without knowing exactly what he was going to get, but who never stopped being a giant. It was a path that involved the conquer of Ms Go's self-confidence, however, still today, I find it hard to understand why he constantly believed in me. His presence has been more important than what I will ever be able to show him. Fortunately, this giant was frequently side by side with three other giants, Costanza Cucci, Andrea Casini and Lorenzo Stefani, always extraordinary at giving me time when they did not have it. One giant, Vanessa Otero, who was always my biggest role model and who, on a path in which work mingled with friendship, is the reason of everything done well in this thesis. One giant, Professor Jorge Parola, who helped to relativise what sometimes, and unfairly, seemed to be the end of the world. To these three giants supervisors, I am wholeheartedly grateful for the opportunity, in general, and for all the opportunities, in particular, after mistakes, fears, doubts, insecurities, disappointments and, even, some apathy. In so many moments, characterised by these feelings, I did not celebrate this work. However, it was always an enormous honour to have you as my supervisors. I was a lucky one.

Giants who, in its whole, are known as Family and, in particular, are known as Mum, Dad, Diogo, Tiago, Grandma Lina, Mariana, Filipa, Isabel, Aunt Ana, Mário and Sérgio. And one giant so so enormous and special that he could not fit on Earth anymore and ended up going to Heaven, who is known as Grandpa Zé. *Grandpa, it is not the type of doctor you would think, yet, in the end, you will have a granddaughter who is a doctor.*

Another giant, Tiago, who appeared in this difficult path and - so it seems - came to stay, making one believe that, for that reason only, the journey was worth it. Fortunately, he did not come alone and brought Isa, António and Ricardo with him.

Giants who, in its whole, are known as Friends and, in particular, are my Venn's Diagram, Andreia Mendes and Raquel Marques, my Number 1, Catarina Geraldês, my wholehearted friends, Joana Devesa and Francisca Lourenço, and my babes, Daniela Pinto and Magda Viana. Others, who started as colleagues and ended up being the giants Inês Soares, Márcia Vieira, Paula Nabais, Artur Neves and Rita Araújo. Also, those who turned Florence into a second home, Paola Di Ninni, Letizia Di Bartolo, Filippo Cherubini, Filippo Micheletti, Italo Celiento, Alessio Dezi, Marco De Vita and Francesca Martemucci.

Others, whose words, behaviour and time given, momentary or sporadic, also allowed to see further: Ana Maria, Isabel Pombo Cardoso, Professor Leslie Carlyle, Professor Joana Lia, Professor Maria João Melo, Julio del Hoyo-Meléndez, Antoine Stopin, Cristina Montagner, Élia Roldão, Juliana Buse, Giovanni Bartollozi, Marilena Ricci, Maurizio Becucci and Professor Victor de Freitas. Also, the girls at DCR and people at the Photochemistry Lab; the students and colleagues who, in some moments, became much more than that; the colleagues within COSCH project; and everyone who eventually crossed this path and made it more complete, happier or less tiring, whose names are missing, because it has been a long journey and the memory starts to fail.

To all the giants, more than the certainty that you supported a PhD, it remains certain that you supported the growth, learning, development and strengthening of this person, both professionally/academically and personally speaking. One day, I heard someone saying, about PhDs, that any resemblance between the final thesis, the initial project and the plans made is merely a coincidence. This being true, this thesis was not an exception. A lot remained to be researched, discovered and created. From one question made, two questions were born, and three questions remained unanswered. However, today, I am more complete, braver, more resilient and - maybe - a little less ignorant. This thesis, itself, is the proof of all of that. It is ready to be redone and if I could do it again I would do it differently. I would do it gigantically better.

Finally, I am grateful to DCR/FCT-UNL and to IFAC-CNR, and to all the people that make these institutions, and I am grateful to the Foundation for Science and Technology and to the Doctoral Programme CORES (PD/00253/2012), for the PhD grant PD/BD/105902/2014 that allowed me to climb this step from where, feeling lucky, I stare with pride and wonder at all the giants.

# Resumo

Palavras-chave: cochinha, ácido carmínico, Winsor & Newton, reconstruções, caracterização multi-analítica, envelhecimento artificial

Os pigmentos laca de cochinha pertencem a uma importante classe de materiais para artistas sensíveis à luz, que requer especial atenção. O seu desvanecimento provoca alterações indesejáveis na aparência visual das obras de arte e a sua identificação é uma tarefa especialmente desafiante. Neste trabalho, foram estudados os processos de manufatura de pigmentos laca de cochinha do arquivo do século XIX da Winsor & Newton (W&N), uma fonte primária no que concerne às práticas de um dos fabricantes de materiais para artistas mais importantes na altura. Foram estudados quatrocentos e quarenta e três (443) registos relativos aos produtos de cochinha, *Carmin* (28%), *Crimson* (30%), *Scarlet* (22%) e *Purple* (20%), os quais demonstram a dedicação e compromisso da W&N em relação à qualidade e durabilidade dos seus pigmentos. Desses 443 registos, foram identificados dois métodos de síntese principais, cuja diferença reside no pH de extração. Sete processos de manufatura representativos foram selecionados e reconstruídos com a maior exatidão possível e a maior parte dos pigmentos resultantes foram comparados, com sucesso, a amostras históricas. Foi utilizada uma abordagem multi-analítica, que incluiu ICP-AES,  $\mu$ EDXRF, UV-Vis-NIR FORS,  $\mu$ Espetrofluorimetria,  $\mu$ FTIR,  $\mu$ Raman e SERS, para caracterizar as reconstruções e as amostras históricas, tendo sido possível detetar diferentes cromóforos. Cada um destes cromóforos apresenta uma impressão digital elementar e molecular que é ainda caracterizada por um aluminato, gesso ou pigmento inorgânico (vermelhão), característicos dos processos de manufatura da W&N. A evidência experimental sugere, pela primeira vez, que a presença de alumínio e cálcio na estrutura molecular é essencial para obter complexos organizados, os quais correspondem a pigmentos carmin. Por sua vez, a ausência de cálcio resulta muito provavelmente numa mistura de isómeros de complexos mais pequenos e tons arroxeados. Reconstruções selecionadas e amostras históricas pintadas com goma-arábica e poli(acetato de vinilo) foram também sujeitas a uma experiência de envelhecimento acelerado com luz utilizando uma *solabox*. Estas amostras foram estudadas com técnicas analíticas convencionais e com espectrometria *microfading* e imagiologia hiper-espectral de refletância no Vis-NIR, contribuindo para demonstrar as potencialidades destas duas técnicas relativamente inovativas. No geral, as referências de carmin revelaram-se as mais estáveis quando misturadas com goma-arábica, enquanto o pigmento escarlata com poli(acetato de vinilo) mostrou uma ligeira menor alteração de cor quando comparado com a quase total perda de cor das restantes tintas com poli(acetato de vinilo). Este trabalho permitiu alcançar um importante avanço e obter um significativo conjunto de materiais de referência e informação espectral que permitem dar continuidade ao estudo de pigmentos laca de cochinha, da sua fotodegradação e da sua identificação em obras de arte.



# Abstract

Keywords: cochineal, carminic acid, Winsor & Newton, historically accurate reconstructions, multi-analytical characterisation, artificial ageing

Cochineal lake pigments belong to an important class of light-sensitive artists' materials that requires particular focus. Their fading results in undesirable changes in the artworks' visual appearance and their identification is a challenging task. In this work, the Winsor & Newton (W&N) 19th Century Archive Database, a primary source on the practices of one of the leading artists' colourmen at that time, was investigated in relation to their manufacturing processes for cochineal lake pigments. Four hundred and forty-three (443) production records pertaining to Carmine (28%), Crimson (30%), Scarlet (22%) and Purple (20%) cochineal products were studied, which revealed the commitment that W&N made to the quality and durability of their pigments. Two main methods of synthesis were identified, which difference lies on the pH of extraction. Seven selected representative manufacturing processes were reconstructed with as much historical accuracy as possible and the majority of the resulting pigments were successfully compared with historical samples. A multi-analytical approach, which included Inductively Coupled Plasma Atomic Emission Spectrometry, microEnergy Dispersive X-ray Fluorescence Spectrometry, UV-Vis-NIR Fibre Optic Reflectance Spectroscopy, microspectrofluorimetry, microFourier Transform Infrared Spectroscopy, microRaman Spectroscopy, and Surface Enhanced Raman Spectroscopy, was used to characterise the reconstructions and historical samples. Different chromophores were detected, each presenting an elemental and molecular fingerprint that can be further characterised by an amorphous aluminate, extender (gypsum) or inorganic pigment (vermilion), which are characteristic of W&N's manufacturing processes. Experimental evidence suggests, for the first time, that the presence of aluminium and calcium in the molecular structure is essential to obtain organised complexes which correspond to bright carmine pigments, while the absence of calcium most probably results in a mixture of isomers of smaller complexes and purplish hues. Selected reconstructions and historical samples painted with gum-arabic and poly(vinyl acetate) were also subjected to an accelerated light ageing experience using a solarbox. These samples were investigated with conventional analytical techniques as well as with microfading spectrometry and Vis-NIR reflectance hyperspectral imaging, contributing to the demonstration of the potentialities of these relatively innovative techniques. Overall, the carmine references turned out to be the most lightfast when mixed with gum-arabic while the scarlet pigment with poly(vinyl acetate) showed a slightly smaller colour change when compared with the almost complete loss of colour of the other poly(vinyl acetate) paints. This work has provided an important breakthrough together with a valuable set of reference materials and spectral data for the further study of cochineal lake pigments, their photodegradation and identification in artworks.



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# Symbols and Acronyms

|                                   |                                                                                         |
|-----------------------------------|-----------------------------------------------------------------------------------------|
| $\lambda$                         | Wavelength                                                                              |
| $\nu$                             | Stretching vibration                                                                    |
| $\delta$                          | Bending vibration                                                                       |
| $\Delta E_{ab}$ , $\Delta E_{76}$ | Colour difference calculated using the CIELAB formula                                   |
| $\Delta E_{00}$                   | Colour difference calculated using the CIEDE2000 formula                                |
| $\mu$ EDXRF                       | MicroEnergy Dispersive X-ray Fluorescence Spectrometry                                  |
| $\mu$ FTIR                        | MicroFourier Transform Infrared Spectroscopy                                            |
| $\mu$ Raman                       | MicroRaman Spectroscopy                                                                 |
| $\mu$ spectrofluorimetry          | MicroSpectrofluorimetry                                                                 |
| BW                                | Blue Wool                                                                               |
| CIE                               | Commission Internationale de l'Eclairage                                                |
| CT                                | Charge-transfer                                                                         |
| DCR FCT NOVA                      | Department of Conservation and Restoration of the NOVA School of Science and Technology |
| DFT                               | Density Functional Theory                                                               |
| FORS                              | UV-Vis-NIR Fibre Optic Reflectance Spectroscopy                                         |
| GA                                | Gum-arabic                                                                              |
| HART                              | Historically Accurate Reconstructions Techniques                                        |
| HPLC-DAD                          | High Performance Liquid Chromatography equipped with Diode Array Detector               |
| HSI                               | Vis-NIR Reflectance Hyperspectral Imaging                                               |
| ICP-AES                           | Inductively Coupled Plasma Atomic Emission Spectrometry                                 |
| IFAC-CNR                          | "Nello Carrara" Institute of Applied Physics, National Research Council                 |
| JND                               | Just Noticeable Difference                                                              |
| $K_a$                             | Acidity Constant                                                                        |
| LANBOZ                            | Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects            |
| LPD                               | Lake Pigment Dispersion                                                                 |
| MSI                               | Multispectral Imaging                                                                   |
| MNAC                              | National Museum of Contemporary Art - Museum of Chiado                                  |
| n.a.                              | Not Analysed                                                                            |
| NMR                               | Nuclear Magnetic Resonance Spectroscopy                                                 |
| PCA                               | Principal Component Analysis                                                            |
| PGP                               | Prism-Grating-Prism                                                                     |
| PVAc                              | Poly(vinyl acetate)                                                                     |
| QTH                               | Quartz Tungsten Halogen                                                                 |

|      |                                     |
|------|-------------------------------------|
| RGB  | Red Green Blue                      |
| RE   | Researcher's Edition                |
| ROI  | Region of Interest                  |
| SERS | Surface Enhanced Raman Spectroscopy |
| URC  | Unique Recipe Code                  |
| W&N  | Winsor & Newton                     |

# Chapter 1

## General Introduction

This first chapter starts with a preamble which introduces the context of this doctoral thesis, the research aims and process, and the structure of the thesis. The preamble is followed by a sub-chapter that presents a literature review of the history of cochineal and its main dye, carminic acid. This section also includes the definition of lake pigment and a literature review of cochineal lake pigments.

### 1.1. Preamble

The nineteenth century was a period of research, discovery and innovation. Chemistry became a scientific field and new elements, chemical reactions and compounds were discovered, which had a remarkable influence in the field of art and the expansion of the range of artists' pigments<sup>1</sup> available. One significant breakthrough was the appearance of a new class of coloured materials -

---

<sup>1</sup> The terms pigment, dye (or dyestuff), colourant and chromophore will be used throughout this thesis. Their definition are as follows. Pigments and dyes are commonly distinguished based on their solubility in a binding medium such as gum-arabic or oil to form a paint: pigments are usually inorganic compounds which are insoluble and dispersed in the media, while dyes (or dyestuffs) are generally organic compounds (molecules containing backbones of carbon atoms) that are soluble in the media (Melo et al. 2016). A colourant can be defined as "any compound, such as a dye or pigment, that gives colour to another material" ("CAMEO. Conservation & Art Materials Encyclopedia Online" 2018, Colorant). A chromophore is "the part (atom or group of atoms) of a molecular entity in which the electronic transition responsible for a given spectral band is approximately localised."; the term referred originally to the groupings in the molecule that are responsible for its colour ("IUPAC. Compendium of Chemical Terminology, 2nd Edition (the 'Gold Book')," n.d., C01076).

that of synthetic organic colourants - as a result of the developments in organic chemistry.<sup>2</sup> Not only that, an unparalleled change in the production and accessibility of artists' materials was observed. There was a rise and proliferation of artists' manufacturers and suppliers, known as colourmen, who began to make and provide the materials that had once been prepared by the artists themselves (Bomford et al. 1990, pp.51-55).



**Figure 1.** Vegetable (madder roots, brazilwood) and animal (cochineal insects, kermes insects, lac resin) sources of natural organic red dyes.

Before the emergence of synthetic organic colourants and their use as artists' materials in the nineteenth century, organic colourants had been obtained from natural vegetable or animal sources. The roots of madder and brazilwood trees together with the cochineal, kermes and lac insects were the most common sources of natural red dyes, **Figure 1**. These organic colourants had been in use since antiquity for many applications. They were used to dye textiles and to produce organic pigments - the so-called lake<sup>3</sup> pigments - that could be applied for painting on different supports such as canvases and illuminated manuscripts. Made by combining the dye with an inorganic substrate, creating a complex between the organic molecule and inorganic metal ions such as aluminium(III) or tin(IV), these lakes of striking colour constituted for a long time one large and important class of traditional artists' materials. In the 19th century, lake pigments, particularly reds, were highly prized for their use as transparent glazes or in opaque mixtures with other pigments, for example, lead white, vermilion and blues. It was not until the end of the century that these materials prepared from natural sources were almost completely replaced by the flowering of the new class of synthetic organic colourants (Bomford et al. 1990).

Along with madder, cochineal was the main source of red lakes in the nineteenth century, which were available in many varieties and shades of colour, from pure reds to deep purples (Bomford et

<sup>2</sup> It was in 1856 that the first synthetic organic colourant with no natural equivalent was discovered by chance by a Scottish chemist, William Henry Perkin (1838-1907), while working with aniline, a by-product of coal tar. It was a purple dye known as mauveine, the synthesis of which was the precursor of the synthetic dyes industry (Sousa et al. 2008). Later, in 1868, the first synthesis of an artificial form of a natural dye by two German chemists, Carl Graebe (1841-1927) and Carl Liebermann (1842-1914), took place (Bomford et al. 1990, p.54). The two chemists synthesised alizarin (1,2-dihydroxyanthraquinone), one of the colouring matters of the roots of the madder plant (*Rubia tinctorum*).

<sup>3</sup> The name lake comes from the Latin *lacca* that derives from the much earlier term *laksha* used for the lac insect (*Kerria lacca*), which was known in eastern Mediterranean regions in very early times, and its use spread westwards following the Arabic conquests along the Mediterranean. *Lacca* also came to be used for the red pigment prepared from the insect's dye and was subsequently applied to the similar red pigments made from other sources, such as kermes (*Kermes vermilio*). Until the eighteenth century, the name lake used without qualification indicated a dark red pigment of intense colour and transparency, characteristics that are generally associated with a traditional lake pigment (Kirby, van Bommel, and Verhecken 2014, p.70).



**Figure 2.** *Janellas do pescador*, 1915, oil on canvas, Amadeo de Souza-Cardoso. Museum Calouste Gulbenkian, Lisbon.

(1840-1926), Pierre-Auguste Renoir (1841-1919) and Vincent van Gogh (1853-1890) (Bommel, Geldof, and Hendriks 2005; Pozzi et al. 2014). They were also used by the Portuguese Modernist artist Amadeo de Souza-Cardoso (1887-1918) (Vilarigues et al. 2008; Montagner 2015), **Figure 2**.

Despite their paramount importance in the artists' palette, red lake pigments, particularly cochineal, were associated with light-sensitive materials (Saunders and Kirby 1994a).<sup>4</sup> The fading and colour changes of these pigments have resulted in undesirable changes to the appearance of artworks, which differs from the artists' original intention. Since often these changes are not recognised nor taken into account when viewing the objects nowadays, they can result in a dramatic transformation in the way the artworks are interpreted. The impermanence of cochineal lakes and the impact that their fading may have on the way artworks look today is exemplified by the painting *Madame Léon Clapisson* (Pierre-Auguste Renoir, 1883, oil on canvas, The Art Institute of Chicago, Chicago), which shows fading of the red cochineal lake pigment across the background, while its original colour was preserved along the edges where the painting was protected from light by the frame (Pozzi et al. 2014; Groom and Shaw 2014). A digitally recoloured visualisation of the painting has been presented along with the image of the painting as it looks now by Groom and Shaw 2014, **Figure 3**. Another example is the painting *Red cabbages and onions* (Vincent van Gogh, 1887-1888, oil on canvas, Van Gogh Museum, Amsterdam), **Figure 4**, which greyish-blue background was originally purple due to the fading of a tin-based cochineal paint combined with other paints (Bommel, Geldof, and Hendriks 2005). Saunders and Kirby 1994a and Burnstock, Lanfear, et al. 2005 have shown that tin-based cochineal products are less lightfast<sup>5</sup> than aluminium-based

<sup>4</sup> In the nineteenth century context, cochineal lake pigments were considered less lightfast than madder (Field 1835, p.97; Saunders and Kirby 1994a; Carlyle 2001, p.507).

<sup>5</sup> Lightfastness is the ability of a colourant to maintain its colour when exposed to light, i.e. the degree to which a colourant resists fading or colour change due to light exposure ("CAMEO. Conservation & Art Materials Encyclopedia Online" 2018, Lightfastness).

cochineal lakes.

These two examples presented demonstrate the importance of the identification of light-sensitive materials in artworks, including the characterisation of their chemical composition and an understanding of their ageing processes. This contributes to disclose the original

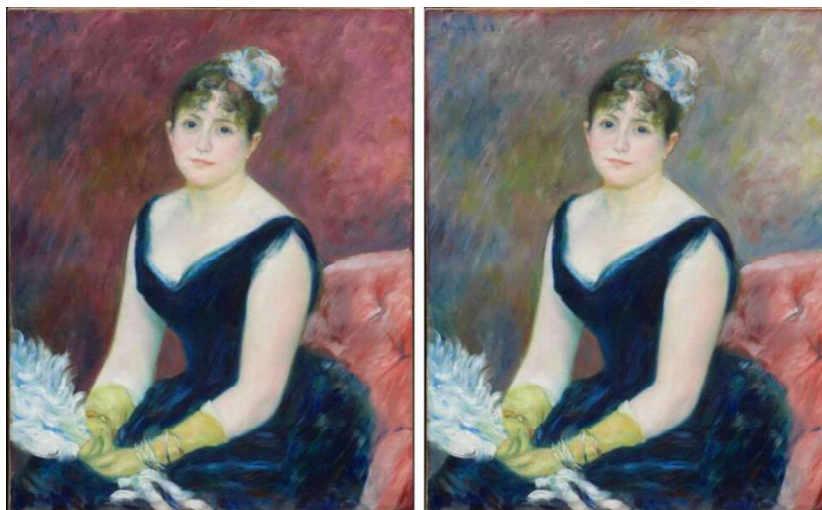


**Figure 3.** *Madame Léon Clapisson*, 1883, oil on canvas, Pierre-Auguste Renoir. Digitally recolourised visualisation of the painting (left) vs image of the painting as it looks now (right). Figure from Groom and Shaw 2014.

colour palette used by the artists and to understand their original intent. It supports the assessment of the condition of the artworks, through the recognition of changes that may be observed, and the planning of appropriate conservation strategies. It can also contribute to their authentication and contextualisation while supporting the estimation of the period of production of the objects and providing information on the resources and technology available to the artists in that period. Understandably, a great amount of attention has been paid to red lake pigments and paints within the field of conservation science and their use and fading in artworks have been the focus of many papers (Saunders and Kirby 1994a; Kirby 2005; Kirby, Spring, and Higgitt 2005; Kirby, Spring, and Higgitt 2007; Burnstock et al. 2005; Bommel, Geldof, and Hendriks 2005; Berg et al. 2006; Clementi et al. 2009; Leonard 2012; Berrie and Strumfels 2017; Centeno et al. 2017).

The identification of these traditional artists' materials in artworks using the analytical techniques most commonly applied in the field is, however, a known challenge. This is so not only due to the complexity of their chemical composition, which is variable depending on the many manufacturing processes available to produce the pigments and in which the dye is usually present in low concentrations, but also as a consequence of the nature of application of the paints and the



**Figure 4.** *Red cabbages and onions*, November 1887-February 1888, oil on canvas, Vincent van Gogh. Van Gogh Museum, Amsterdam (Vincent van Gogh Foundation).

ageing processes. The in situ<sup>6</sup> elemental technique microEnergy Dispersive X-ray Fluorescence Spectrometry ( $\mu$ EDXRF) does not allow identification of the dye. The in situ molecular techniques microspectrofluorimetry ( $\mu$ spectrofluorimetry) and UV-Vis-NIR Fibre Optic Reflectance Spectroscopy (FORS) require the existence of a database of reference materials for comparison. The latter usually lacks specificity to enable discrimination between different red lake pigments (particularly between cochineal, kermes and lac, which are all animal sources) and the characteristic spectral bands obtained are tremendously affected by the nature of application of the paints (Bisulca et al. 2008). For example, dark and opaque paints present a strong absorption with uncharacteristic spectral features, without the degree of detail necessary for fingerprinting unknown materials. On the other hand, recent developments that combined the use of  $\mu$ spectrofluorimetry and chemometrics have enabled the discrimination of dark reds to pink colours based on brazilwood, cochineal, kermes and lac dye (Nabais et al. 2018). The micro-sampling molecular techniques microFourier Transform Infrared Spectroscopy ( $\mu$ FTIR) and microRaman Spectroscopy ( $\mu$ Raman) have their drawbacks; while the first technique often identifies the inorganic component (and possibly the binder) without detecting the dye, the Raman signals are masked by fluorescence which is usually characteristic of lake pigments. The destructive micro-sampling molecular techniques, High Performance Liquid Chromatography equipped with Diode Array Detector (HPLC-DAD) and Surface Enhanced Raman Spectroscopy (SERS), have also been used. However, in most of the cases, they require hydrolysis and extraction steps which result in the destruction of the pigments' molecular structure.

Indeed, identification of cochineal lake pigments may only be possible with a multi-analytical approach supported by a database built from reference materials which are used for comparison purposes and to test new analytical approaches towards their identification. Moreover, reference materials may allow to study the behaviour and permanence of the cochineal pigments and to relate them with their manufacturing processes and chemical composition. They can also be used to study the respective molecular structures which are not known yet. However, results may not be accurate if such references are based on the artists' materials available today that do not reflect the technology of the past. In other words, it cannot be assumed that modern cochineal lake pigments will necessarily have been produced using the same manufacturing processes used in the nineteenth century, thus they may or may not have a similar composition, structure and permanence. The issue of accuracy of results can be approached through the production of references as close as possible to those available in the nineteenth century, using contemporary recipes and materials appropriate to the time of the recipes. The product of this methodology are reconstructions prepared with as much historical accuracy as possible, referred to as historically accurate reconstructions, which are well characterised and validated as accurate references through analytical comparison with historical artists' materials (Carlyle 2018).

In this context, the scope of this doctoral thesis was the study of 19th century cochineal lake

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<sup>6</sup> The term in situ as it is applied in this thesis refers to the analytical techniques which can be used directly on the artworks - with or without contact - without the need to micro-sample. For more information regarding the terminology used regarding analysis, the reader is referred to Wouters 2006 and Wouters 2008.

pigments from the English manufacturer and supplier of artists' materials Winsor & Newton (W&N) based on the preparation of historically accurate reconstructions. Winsor & Newton was one of the leading colourmen of the 19th century, known for their full commitment to produce high quality and durable products. They are also distinguished for continuing the use of natural sources, despite the almost complete replacement of materials prepared from these sources by synthetic organic colourants by the end of the 19th century. Moreover, W&N's archive database has been proven to be a unique and extremely valuable source for the study of 19th century artists' materials (Carlyle et al. 2011; Otero et al. 2012; Vitorino et al. 2016; Otero, Pinto, et al. 2017; Otero et al. 2017). This work was therefore motivated by the willingness to create reference materials of cochineal lake pigments based on a relevant source that can contribute to the knowledge, identification and conservation of these artists' materials in artworks, at the same time proving insight about W&N's manufacture of cochineal products.

The thesis starts with a chapter on cochineal, including a literature review of carminic acid and cochineal lake pigments (Chapter 1). A step by step approach was then used, which initiated with documentary research for W&N's cochineal products (Carmine, Crimson Lake, Scarlet Lake and Purple Lake) on the W&N 19th Century Archive Database, followed by the selection of the most representative manufacturing processes (Chapter 2). The selected processes were reconstructed and characterised with a multi-analytical approach and, whenever possible, the reconstructions were validated as accurate reference materials through comparison with historical samples of cochineal pigments and tubes of oil paint from W&N (Chapter 3). The multi-analytical approach included ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry),  $\mu$ EDXRF, FORS,  $\mu$ Raman,  $\mu$ FTIR, SERS ( $\lambda_{exc} = 633 \text{ nm}$ ) and  $\mu$ spectrofluorimetry. Chapter 3 also details the characterisation of carminic acid, the main dye present in cochineal lake pigments, in solution using absorption and fluorescence spectroscopies. Finally, selected references were subjected to artificial light ageing, which results were followed by FORS,  $\mu$ FTIR,  $\mu$ spectrofluorimetry and colorimetry, as well as by microfading spectrometry and Vis-NIR reflectance hyperspectral imaging (HSI) (Chapter 4). In the end, a general review of the thesis, together with conclusions and further work are presented (Chapter 5).

## 1.2. Cochineal, its dyestuff and lake pigments

The present section of this thesis owes much to the work of important authors, particularly Dominique Cardon and her *Natural Dyes. Sources, Tradition, Technology and Science*, and Jo Kirby, and co-authors, with her extensive research on lake pigments. Besides these references and all those cited throughout this chapter, other works on cochineal exist, which were not consulted in detail, such as Ana Serrano's doctoral thesis, *The Red Road of the Iberian Expansion: Cochineal and the Global Dye Trade*, and the work of Carmella Padilla and Barbara C. Anderson, *A Red Like No Other. How Cochineal Colored the World*.

In the nineteenth century, cochineal was one of the most important sources for artists' lake pigments (Bomford et al. 1990, p.70; Kirby and White 1996). Its history of use as source for colour, however, dates



**Figure 5.** Dried cochineal insects from Kremer Pigmente GmbH & Co. KG, Aichstetten, Germany (36040, *Coccus cacti*, silvery gray).

back to a long time ago. Elena Phipps, in her *Cochineal Red. The Art History of a Color*, describes cochineal as “a humble insect with a long and glorious history, and the treasures dyed and painted with its brilliant red hues bear witness to the contribution it has made to art and commerce throughout the world from antiquity to modern times” (Phipps 2010, p.46).

Cochineal (**Figure 5**), *Dactylopius*<sup>7</sup> *coccus* (O. Costa, 1835), also known as *Coccus cacti*, member of the family Coccoidea, is a scale insect, so named from the hard or waxy scale or other protective covering secreted by the insect (Kirby 1977; Cardon 2007, p.620).

According to Cardon, the name cochineal comes from the Spanish *cochinilla*, derived from the Latin *coccum*, the word used by Pliny in his *Natural History* for kermes, one of the oldest source of red dye (Cardon 2007, p.619). Cochineal's main dye, the anthraquinone carminic acid, is extracted from the dried bodies of the wingless female cochineal scale insects, which are parasites of certain plant hosts, for example, the nopal cactus, *Opuntia* and *Nopalea*. (Kirby 1977; Dapson 2007). After mating with winged males, females give birth to nymphs that are airborne transported by the wind to new host plants (Lecocq 2018). The body of the adult female insect is around 6 mm long, 4.5 mm wide and 4.2 mm high, elliptical in shape, becoming obovate when the female is fully developed (Cardon 2007, p.620). One adult cochineal insect can weigh up to 46 mg, about 70% of which is lost when the insect is dried (Cardon 2007, pp.621-622).

Cochineal was originally found in two principal regions of Central and South America (frequently referred to as the New World): the Peruvian Andes and Mexico. It is known that it was used to dye textiles at least since the time of the Peruvian Paracas culture, 700 B.C., and it was used by the Aztec, Incan and Mayan people (Schweppe and Roosen-Runge 1986; Cooksey 2018). By the sixteenth century, when the Spanish arrived at the New World, the cultivation of the insect for dyeing textiles and for painting, to colour women's body, and as medicine and cosmetic was well established particularly in Mexico (Greenfield 2005; Cardon 2007, pp.621,631,632; Kirby, Spring, and Higgitt 2007). The Spanish recognised the similarity between cochineal and the European kermes<sup>8</sup> and called it *grana cochinilla* (Schweppe and Roosen-Runge 1986), **Figure 6**. Two types

<sup>7</sup> *D. coccus* Costa is the domesticated species of the *Dactylopius* genus which comprises ten species (Serrano et al. 2013).

<sup>8</sup> For centuries, well before the discovery of America, insects living in Europe and the East were used to obtain red colours for dyeing textiles and produce pigments. Kermes, *Kermes vermilio*, a scale insect found on, for example, the kermes oak, *Quercus coccifera*, was one of the oldest, most prestigious and important source of dye. It is found typically in limestone coastal regions around the Mediterranean in Spain, southern France, North Africa and in the eastern Mediterranean. It was called by the Spanish *grana para tefir* and *grana in grano*, from grains or berries (Merrifield 1967, p.clxxiv). Its dye consists mainly of kermesic acid, the aglycone of carminic acid. (Kirby 1977; Schweppe and Roosen-Runge 1986; Kirby, van Bommel, and Verhecken 2014, pp.9-12)

of cochineal are described, the cultivated or domestic fine cochineal (*grana fina*, also known as *nocheztli*, the “blood of the nopal”), *Dactylopius coccus*, and the wild cochineal (*grana silvestra*), the first type being more valuable and richer in colouring matter (Perkin and Everest 1918, p.76; Donkin 1977; Schweppe and Roosen-Runge 1986; Greenfield 2005, p.40). The main centre for cultivation of cochineal was Mixteca, a southern Mexican province, the name of which influenced the terms *mestèque* and *mesteeck* later used in Europe for the best quality of *grana fina* (Cardon 2007, p.629). Oaxaca is also referred to as an important cochineal-producing region (Donkin 1977; Greenfield 2005, p.36; Salinas 2018).

Cochineal insects were harvested from the host cacti,

**Figure 7**, before the

commencement of the rainy season, and brushed into straw baskets or basins of tinned iron (Perkin and Everest 1918, p.76). The female insects were collected mature, at an age of 90 - 110 days, just before egg-laying began, when the concentration of dye is at its highest (Lloyd 1980). Some insects were left upon each cactus, so that a new generation would be produced, which would then be again gathered at a suitable period (Perkin and Everest 1918, p.76). Cardon and Donkin relate different types of cochineal according to the methods used to kill and dry the insects harvested from the cacti (Donkin 1977; Cardon 2007, p.623). The earliest and simplest, but also the slowest, method was to spread them on mats placed in the sun. This method was considered to be the best, producing a fine silver cochineal. Another option was to dry the insects in an oven at a moderate heat, the result of which was an ash grey cochineal. The insects could be also heated on sheets of hot metal, giving black cochineal, or steamed or immersed in boiling water and then dried in the sun giving a product considered inferior in quality.



**Figure 6.** The nopal plant that is grown in America and produces grana from *Reports on the History, Organization, and Status of Various Catholic Dioceses of New Spain and Peru* (1620-49). Figure from Phipps 2010, p.4.



**Figure 7.** Engraving of a Mexican *nopalery* (plantation of nopal cacti) in the eighteenth century entitled *The Manner of Propagating, Gathering and Curing ye Grana or Cochineal, Done by an Indian in the Bishoprick of Guaxaca in the Kingdom of Mexico in America* from Sloane 1725. Figure from Schweppe and Roosen-Runge 1986.

Cochineal was introduced in Europe after the conquest of the Aztec Empire by the Spanish conquistador Hernan Cortes in 1521 (Salinas 2018). It was imported, by the Spanish, from the early sixteenth century onwards, and began to be used for dyeing and painting, gradually supplanting the local sources of red colour, such as kermes, Polish and Armenian scale insects<sup>9</sup> and lac (*Kerria lacca*), due to its higher colourant content and better quality (Kirby 1977; Cardon 2007, pp.631,632; Kirby, van Bommel, and Verhecken 2014,

pp.9-12). Cardon and Cabral refer that the first cochineal cargoes to arrive in Spain date from 1523 (Cardon 2007, p.630; Cabral 2013). In 1542 it was being used in Italy and in the 1560s it was available in London (Cabral 2013). The domestic variety of cochineal was that destined for export and commercially available and the insects were apparently imported in dried form. The Spanish are said to have prohibited the export of live insects from the New World so that they could preserve a highly lucrative monopoly in cochineal which they were able to maintain up to 1820 (Harley 2001, p.136; Kirby, Spring, and Higgitt 2007; Salinas 2018). Indeed, apart from precious metals such as gold and silver, cochineal became one of the most valuable and substantial export commodities (Donkin 1977; Kirby, Spring, and Higgitt 2007). Phipps states that, according to Jose de Acosta, a Spanish naturalist who recorded the flora and fauna of Peru, the shipments to Spain in 1587 included about 72 tons of cochineal (Phipps 2010, p.27).

In the late eighteenth century, beginning of the nineteenth century, many attempts were made to establish plantations of the nopal cactus and raise the cochineal insects in different parts of the

<sup>9</sup> Along with kermes, other scale insects are known to have been used in Europe and the East. The most familiar of these insects is the Polish cochineal insect, *Porphyrophora polonica*, found in sandy regions of central and eastern Europe, including Poland, parts of Germany, the Czech Republic, Hungary, Ukraine and Russia and further east into Mongolia, and the Armenian or Ararat cochineal, *Porphyrophora hamelii*, found in the plain of the Araks river at the foot of Mount Ararat, Armenia (Kirby 1977; Kirby, van Bommel, and Verhecken 2014, pp.9-12). These Old World cochineals were an even more expensive and slightly more blue-toned crimson dye (Kirby, van Bommel, and Verhecken 2014, pp.9-12). Polish cochineal is now preferably called Polish crimson-dyeing scale insect, or carmine scale insect, and Armenian cochineal is preferably called crimson-dyeing scale insect (Cardon 2007, p.636). *Porphyrophora polonica* has historically been also known as Polish kermes (Schweppe and Roosen-Runge 1986; Eastaugh et al. 2004, p.119 citing Rosetti 1548).

world in order to break the Spanish monopoly of cochineal (Cardon 2007, p.621). The economic implications in the nineteenth century were enormous, given the growing importance of, and worldwide demand for, dye products in general, and cochineal in particular. Using Greenfield's own words, "In England, the Netherlands, and France, the search for cochineal soon took on the tone of a national crusade. Kings, haberdashers, scientists, pirates, and spies - all became caught up in the chase for the most desirable color on Earth." (Greenfield 2005, p.4). Outside Mexico, other countries in Central and South America developed their cochineal production and export industries: Guatemala - the most important, according to Cardon -, Honduras, Nicaragua, El Salvador, Peru, Bolivia and Chile (Cardon 2007, p.631; Kirby, Spring, and Higgitt 2007). Ure observed that in 1852, the Honduras cochineal was more expensive than the Mexican cochineal (Ure 1870, p.452). Trying to regain control, the Spanish introduced cochineal cultivation in the Canary Islands, which production became the most important in the world. Schweppe and Roosen-Runge observed that the Canary Islands were leading in cochineal export in 1869 with 2717 tons while Lloyd claims that "a peak of over 3000 tonnes in 1875" was reached (Lloyd 1980; Schweppe and Roosen-Runge 1986). The French also created cochineal plantations in Algeria, and a Dutch colony was established in Java, Indonesia (Kirby, Spring, and Higgitt 2007).

Schweppe and Roosen-Runge (1986) describe the different types of cochineal commercially available during the nineteenth century when cochineal was at the height of its use:

- (1) Honduras cochineal, which was shipped directly to England, included three varieties: black cochineal; grey, spotted, or silver-coloured cochineal; and red cochineal;
- (2) Vera Cruz cochineal, imported via Bordeaux and Le Havre;
- (3) Canary cochineal, also called Tenerife cochineal, shipped from the Canary Islands via Cadiz and Marseille;
- (4) Java cochineal, shipped directly to Amsterdam and Rotterdam.

In 1915, Church states that the best quality of cochineal would come from Tenerife (Church 1915, p.207). The worldwide collapse of the cochineal market occurred in the last two decades of the nineteenth century as a result of the emergence of synthetic organic colourants. Today the main producing centres of cochineal are Peru (85 % of world production with 885.9 tonnes), Chile (10.5%), Canary Islands (2.9%) and Bolivia (1.9%) (Cardon 2007, p.631). Listed by the Colour Index<sup>10</sup> (1971) as Natural Red 4, No. 75470, and as colourant E120 by the European Union, it is used as source of colourant for food, pharmaceutical and cosmetic industries and in medicine (Cardon 2007, p.632; Norman et al. 2015).

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<sup>10</sup> The Colour Index is a publication produced by the Society of Dyers and Colourists, England, which provides a comprehensive listing of the known commercial dyes and pigments and is updated on a regular basis. Each colourant is given a C. I. Generic Name, which indicates its application class, hue and a number which reflects the chronological order in which the colourants were introduced commercially. The Colour Index is the most important reference work related with the classification of dyes and pigments. (Christie 2001, p.24)

### 1.2.1. The dyestuff, carminic acid

Carminic acid, **Figure 8**, is the main colourant extracted from cochineal insects. Dried domestic cochineal contains up to 20% carminic acid, which appears in the form of potassium salts (Ishida et al. 1987; Cardon 2007, pp.622,624,709 and references cited therein). The relative composition of cochineal has been studied by Wouters and Verhecken (Wouters and Verhecken 1989 and references cited therein) and Serrano and co-authors (Serrano 2010, p.15; Serrano et al. 2011; Serrano et al. 2013; Serrano et al. 2015; and references cited therein).<sup>11</sup> Carminic acid, ca, accounts for an average of 95% of the colourants present in the insect. Other dyes present in the extracts of cochineal are flavokermesic acid, fk, and kermesic acid, ka (0.2-0.5%), and three colourants referred to by the initials of the scientific name of the insect, dc (*Dactylopius coccus*): a yellow compound, dcII (2.3-2.4%), and two red colourants, dcIV (1.0-1.4%) and dcVII (0.4-1.0%). Cardon, citing the work of Wouters and Verhecken, refers also dcIII, present in varying proportions (0.1-2.4%) or absent in some extracts (Cardon 2007, p.624). The dcII, dcIII, dcIV and dcVII components have been isolated and their structure has been elucidated in the work by Stathopoulou et al. 2013.

Carminic acid has the formula  $C_{22}H_{20}O_{13}$  and is generally described as 7- $\beta$ -D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracene-carboxylic acid, though some authors present it as an  $\alpha$ -D-glucopyranosyl or as C-D-glucopyranosyl (e.g. Ishida et al. 1987; Allevi

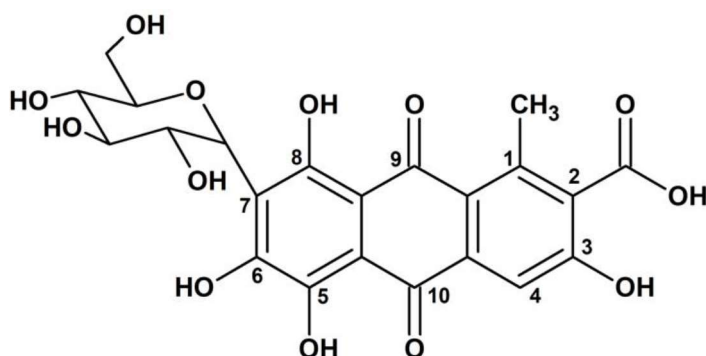


**Figure 8.** Molecular structure of carminic acid.

et al. 1998; Favaro et al. 2002; Ibarra et al. 2005; Cooksey 2018). The structure of carminic acid is derived from 9,10-anthraquinone,<sup>12</sup> which is the basic skeleton of one of the most important and oldest chemical classes of red dyes (Melo 2009). It is a polyprotic acid with one carboxylic and four phenolic groups susceptible to

<sup>11</sup> Studies by the referred authors have shown that it is possible to distinguish between different species of *D. coccus* and *Porphyrophora* despite the similarity of their chemical compositions.

<sup>12</sup> 9,10-anthraquinone contains a characteristic system of three six-membered benzene rings (anthracene) in which two carbonyl groups are in the central ring and the two outer rings are fully aromatic (Christie 2001, pp.70-71). It has the lowest excited singlet state of  $n,\pi^*$  character, being a colourless molecule. Their hydroxy derivatives (hydroxyanthraquinones), however, absorb visible light and are coloured (Miliani, Romani, and Favaro 2000). This is so due to their  $\pi,\pi^*$  excitation energy which is lower than the  $n,\pi^*$  excitation energy of anthraquinone. The carbonyl group,  $C=O$ , is  $\pi$  electron acceptor and the hydroxyl group,  $OH$ , is a powerful  $\pi$  electron donor. The presence of the latter in the anthraquinone ring causes a charge-transfer (CT) electronic transition of relatively low energy corresponding to a  $\pi,\pi^*$  absorption band in the visible region of the spectrum (Suppan 1994, pp.206-207). This CT transition is associated with the transfer of an electron from the electron-donor substituent to the carbonyl group (Diaz 1990). A bathochromic shift of the colour, i.e. a shift of the absorption band to longer wavelength, might be obtained by increasing the electron acceptor and electron donor power and by extending the length of the conjugation (Christie 2001, p.27).

deprotonation plus one methyl group and a glucose moiety. Due to the positioning of its carbonyl and hydroxyl groups, carminic acid is suited to coordination bonding with metal ions (Dapson 2007).

Perkin and Everest and Cardon refer that carminic acid was first isolated in 1818 by the French chemists P. J. Pelletier and J. B. Caventou (Perkin and Everest 1918, p.77; Cardon 2007, p.624). It is also said to have been isolated for the first time in a pure condition by de la Rue in 1847 and to have been first isolated in crystalline form in 1858 by P. Schützenberger (Perkin and Everest 1918, p.77; Schweppe and Roosen-Runge 1986; Allevi et al. 1991). Its structure was first established by the German chemist O. Dimroth, researching between 1909 and 1920, and was later revised in 1959 by M. A. Ali and L. J. Haynes (who established the presence of a glucose unit linked to the anthraquinone by a C-glycoside bond), in 1964 by J. C. Overeem and G. J. M. van der Kerk, and in 1965 by S. B. Bhatia and K. Venkataraman (Perkin and Everest 1918, pp.6,77-88; Ali and Haynes 1959; Lloyd 1980; Schweppe and Roosen-Runge 1986; Allevi et al. 1991; Allevi et al. 1998; Cardon 2007, p.624). Cardon states that the structure of carminic acid was confirmed in 1984 by P. Schmitt and colleagues (Cardon 2007, p.624 citing Schmitt et al. 1984). Allevi et al. 1998 also refer that the  $\beta$  configuration of the C-glycoside bond was proved and confirmed by Fiecchi et al. 1981 and by P. Schmitt et al. in 1984. In turn, Cardon claims that Ishida and co-authors have shown that the  $\beta$  stereochemistry is present in the cochineal insects whereas the  $\alpha$  configuration may be present in synthetic carminic acid (Cardon 2007, p.709 citing Ishida et al. 1987). Carminic acid is reported to have been synthesised for the first time in 1991 (Allevi et al. 1991, 1998).

Currently, carminic acid has a multitude of applications. With its non-toxic, antitumor and antioxidant properties, it is applied in fields such as food, cosmetics and pharmaceutical products (González et al. 2005; Heydari, Hosseini, and Zarabi 2015; Šuleková et al. 2017; Ordoudi et al. 2018). It is also used for the determination of elements such as boron, molybdenum, vanadium, uranium, thorium and tungsten (Callicoat and Wolszon 1959; Pérez-Ruiz et al. 1995; López-Martínez, Guzmán-Mar, and López-De-Alba 2001; Floquet et al. 2016 and references cited therein), as a dispersing agent (Periasamy, Ho, and Chen 2011), sensitizer (Heera and Cindrella 2010; Sun et al. 2016), colourant for rubber objects (Gabrielli et al. 2018), biological stains (Dapson 2005; Dapson 2007; Sabnis 2010, p.88; Cooksey 2018), for dyeing of textiles (Sadeghi-Kiakhani, Safapour, and Mirnezhad 2018), and the preparation of hybrid materials (Norman et al. 2015; Trigueiro et al. 2018; Guillermin et al. 2019).

### 1.2.2. Cochineal lake pigments

Lake pigments, commonly associated to organic pigments, are generally described as translucent pigments made by precipitating or adsorbing the soluble organic dye onto a colourless or white inorganic inert substrate (Clementi et al. 2008). This substrate is traditionally some form of

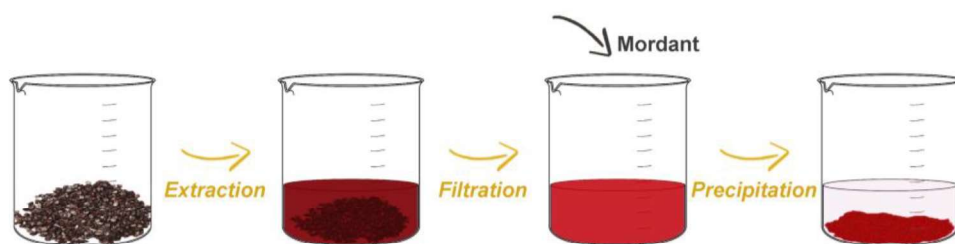


**Figure 9.** Schematic standard procedure to produce lake pigments.

amorphous hydrated alumina<sup>13</sup> and the dye is bound through complexation with metal ions (Kirby, van Bommel, and Verhecken 2014, pp.1,28). Their use is said to date back to the ancient Egyptians, who found a method of dissolving the dye from madder in water and fixing the colour onto a transparent white powder such as chalk or gypsum (Fairbairn and Beal 1982, p.11). However, Ball warns that “we cannot tell if they invented it” (Ball 2008, p.72). The metal ions are commonly called mordant,<sup>14</sup> which link to specific groups of the dye molecule such as neighbouring C=O and OH groups forming metal-dye complexes (Clementi et al. 2008). The most important and common mordant is the aluminium ion,<sup>15</sup>  $\text{Al}^{3+}$ , generally in the form of alum, also known as potash alum or potassium alum<sup>16</sup> (Kirby, van Bommel, and Verhecken 2014, p.25).

A standard procedure to produce lake pigments, **Figure 9**, typical of historical recipes is to extract the dye from the raw material - which is first cut or ground up - in an aqueous solution. The solution

<sup>13</sup> Alumina is the common name for aluminium oxide,  $\text{Al}_2\text{O}_3$  (Atkins and Jones 1997, p.742). Hydrated alumina, alumina hydrate or aluminium hydrate can be defined as aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , a white, gelatinous, light precipitate, that entraps impurities as it settles, widely employed as an inert substrate for lake pigments (Mayer 1991, p.36; Atkins and Jones 1997, p.743). It is prepared from alum and an alkali such as sodium or potassium carbonate. When alum is added to an aqueous solution, it dissociates to give  $\text{Al}^{3+}$  ions, which hydrate to form the hydrated  $\text{Al}^{3+}$  ion  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  (Clementi et al. 2008 citing Omoike and Vanloon 1999). In alkaline solutions, it undergoes hydrolytic reactions to form solid amorphous  $\text{Al}(\text{OH})_3$ , which adsorbs dyestuffs easily:  $2\text{KAl}(\text{SO}_4)_2 + 3\text{K}_2\text{CO}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 4\text{K}_2\text{SO}_4 + 3\text{CO}_2$ . It is used in paint manufacture, largely as a filler, and is the most common cheapening agent for artists' oil colours. Because of its low refractive index, it lacks covering power and lends transparency to colours. (Gettens and Stout 1966, pp.91,92)

<sup>14</sup> The term mordant is derived from the Latin *mordere*, which means “to bite” (Gettens and Stout 1966, p.132).

<sup>15</sup> Aluminium is the most abundant metallic element in the Earth's crust and, following oxygen and silicon, the third most abundant element (Atkins and Jones 1997, p.739). It is amphoteric, reacting both with acids to form aluminium ions,  $\text{Al}^{3+}$ , and with alkalis to form aluminate ions,  $[\text{Al}(\text{OH})_4]^-$  (Atkins and Jones 1997, p.741).

<sup>16</sup> Today the name alum can be used for any hydrated double sulphate with the general formula:  $\text{M}^{\text{I}}\text{M}^{\text{II}}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (where  $\text{M}^{\text{I}} = \text{K}^+, \text{Na}^+, \text{NH}_4^+$ , etc., and  $\text{M}^{\text{II}} = \text{Al}^{3+}, \text{Fe}^{3+}$ , etc.). It can be a double sulphate of aluminium and potassium, or aluminium and ammonium, aluminium and sodium, or mixtures of these (T. F. Glick 2005). Potash alum or potassium alum, one of the most important alums, is a hydrate double sulphate of aluminium and potassium with the formula  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (Graaff 2004, p.16). It is found in its native state in the form of efflorescences or deposits in the cracks of argillaceous or carboniferous rocks containing pockets of white iron pyrites (Cardon 2007, p.21). Procedures for manufacturing alum from the mineral alunite or alumstone or from pyritic shales were already known in antiquity and in medieval times, alum production was a large industry (Cardon 2007, pp.23,27; Ball 2008, p.65). In the nineteenth century, in the United Kingdom (UK), alum factories could be found near Glasgow, Scotland, and in Whitby, England (Ure 1870, p.50-52; Cardon 2007, p.29). UK alum is said to have contained potash as its alkaline constituent (Ure 1870, p.50-52).

is filtered to remove remnants of the dye source and alum is added to the filtered solution forming a complex with the colourant, which is still soluble. The acidic alum-dye solution is then neutralised by means of the addition of an alkali causing precipitation of the lake pigment, i.e. an insoluble metal-dye complex precipitates when a neutral molecule is formed at slightly acidic or neutral pH (Melo et al. 2016). The precipitate is then filtered and washed several times with water to remove the excess material. The alkali could be potassium carbonate, but by the nineteenth century was as likely to be a sodium salt, which was cheaper and manufactured on a large scale. The lake pigment produced by this method is composed of an amorphous hydrated alumina similar to the light alumina hydrate described in modern paint technology literature, in which sulphate anions become incorporated into the substrate as it precipitates. Another procedure to produce lake pigments which concerns mainly earlier historical recipes, used at least until the beginning of the eighteenth century, involves the extraction of dye into an alkaline solution. The dye solution is then filtered, and alum is added, reacting with the alkali to produce an amorphous hydrated alumina substrate which precipitates together with the dyestuff, forming the lake pigment. This form of alumina is gelatinous and highly absorbent when precipitated, therefore if precipitation is rapid, a certain amount of carbonate from the alkali may be brought down as well, whereas the sulphate remains in solution as the potassium salt, which is water-soluble (Kirby 1977; Kirby, Spring, and Higgitt 2005; Kirby, van Bommel, and Verhecken 2014, pp.28-32,77).

During the sixteenth century, when cochineal first came into use in Europe, and until the seventeenth century, cochineal lake pigments were prepared by the method used for lake pigments prepared from kermes, Polish and Armenian scale insects, and madder. This method involved extracting the dye from dyed textile shearings or clippings - which would be less expensive than the raw material itself - using alkali and adding alum to precipitate the dyestuff on a substrate of amorphous hydrated alumina (Kirby, Spring, and Higgitt 2007; Kirby, van Bommel, and Verhecken 2014, pp.32,33). From the seventeenth century onwards, recipes began to appear for cochineal pigments prepared directly from the insects. One example appears in the so-called Paduan Manuscript, which is actually Venetian and dates from the latter part of the sixteenth century or the seventeenth century (Merrifield 1967, p.643). This change in the method of making cochineal pigments was a consequence of three developments occurring in the late sixteenth century, beginning of seventeenth century, and which are described by Kirby, Spring, and Higgitt 2007. The first development, which was apparently a matter of chance, was the discovery in the 1580s by a Franciscan monk in Pisa of a method of precipitating the insect dyestuff, predominantly carminic acid, in the form of a metal complex or salt. The resulting pigment lacks the high proportion of hydrated alumina substrate present in a conventional cochineal lake and became known as carmine. The second development occurred in 1612 when Antonio Neri published a treatise on glass making, *L'arte vetraria*, which also contained some pigment recipes. One of the recipes to make lake pigments from *chermesi* (a name that then signified crimson and Old or New World cochineal), which was invented by Neri in Pisa, involved extraction of the dyestuff from the insects with alcohol and the addition of an aqueous solution of alum to precipitate the pigment, without using the dyed textile. The third development was the introduction of tin salts as mordant in the early seventeenth century.

Kirby, van Bommel, and Verhecken 2014 refer that recipes for tin-containing cochineal pigments are known from the mid-eighteenth century and the pigments became widely used, particularly in the nineteenth century. Unlike alumina-containing cochineal pigments, however, the scarlet pigments made from cochineal with tin salts were opaque and the colour was so intense that starch was frequently added during manufacture, giving a pigment that was just as bright in colour but with slightly improved handling properties and more economical to prepare (Kirby, van Bommel, and Verhecken 2014, p.78).

Cochineal pigments can thus be distinguished into two main types, the carmines and the conventional cochineal lakes. The carmines are described as metal complexes or salts of carminic acid with little or no inorganic substrate. According to literature, they could be made with aluminium or tin (Field 1835, p.100; Kirby, van Bommel, and Verhecken 2014, pp.32,33), aluminium and tin (Hurst 1892, p.251), or aluminium and calcium (Gettens and Stout 1966, p.110; Meloan, Valentine, and Puchtler 1971; Dapson 2005; Kunkely and Vogler 2011). Their preparation, however, was considered a difficult and mysterious art, kept secret by the (few) successful manufacturers, to which certain unexplained conditions played an important role (Ure 1870, p.376; Hurst 1892, p.251; Bersch 1901, p.357; Kirby, Spring, and Higgitt 2007). Citing Hurst, "various descriptions of processes have appeared from time to time; some of these are very misleading, and have probably been intentionally made so" (Hurst 1892, p.251). Writing in 1758, Dossie claimed that the best carmine was prepared in France: "The difference itself between the English and French carmine, which does not lie in the beauty of the colour, but in its durableness and fixt nature, clearly evinces a diversity in the preparation, and leaves no room to doubt, but that the carmine might be equally well made in this country, if we were thoroughly masters of the art. At present we buy of France the far greatest part of what is consumed, which is more than can be easily imagined." (Dossie 1758, pp.54,55). Kirby, Spring, and Higgitt 2007 refer that the preparation of carmine required "the best cochineal, iron-free alum, the purest water, the cleanest vessels, and a sunny day". Cochineal dyestuff could be precipitated from an aqueous solution of the dyestuff by adding cream of tartar and alum, or citric or oxalic acids and alum, or alum and tin(IV) chloride, or various other salts. The remaining solution was often still highly coloured since the whole of the colouring matter of cochineal is not precipitated, which could be used to prepare a conventional cochineal lake (Kirby 2005). Carmines were considered the finest and most expensive red colour (Ure 1870, p.378; Bersch 1901, p.357). According to Tingry (1831), "The lakes most in request are those called carminated (a term derived from carmine...) because they strongly resist the destructive influence of light. Their colouring part is extracted from cochineal. They are imitated with colouring parts extracted from some vegetable substances; but the latter produce generally inferior lakes, their colouring parts being easily altered by the combined action of air and light...they must be entirely banished from the pallet of the painter who sets any value on the opinion of posterity.". Tingry (1831) describes carmine as "this kind of fecula, so fertile in gradations of tone by the effect of mixtures, and so grateful to the eye in all its shades; so useful to the painter and so agreeable to the delicate beauty, is only the colouring part of a dried insect, known under the name cochineal." (Tingry 1831, p.90). Tingry observes that the remaining decoction, after preparing carmine, is still highly coloured and is reserved for the

preparation of carminated lakes (Tingry 1831, p.91). Field wrote that they were “the brightest and most beautiful colours prepared from cochineal, of a fine powdery texture and velvety richness” (Field 1835, p.100), while Church referred that it was “the most concentrated and purest form of any of the pigments derived from this source” (Church 1915, p.207). Ure also added that it was often adulterated with starch (Ure 1870, p.378), whereas Schweppe and Roosen-Runge 1986 indicated that the best and purest type of carmine was called *carmine nacarat*.

As for the other main type of cochineal pigments, that of conventional lakes, references were made to crimson lakes, “a cochineal pigment containing more aluminous base than carmine, and is consequently weaker in colour and less stable” (Eastaugh et al. 2004, p.134 citing Salter 1869, 135); scarlet lakes, described as cochineal lake commonly tinted with vermilion (Field 1835, p.99) or a mixture of crimson lake and vermilion (Church 1915, p.208); and purple lakes, reported to be more durable than crimson lakes though it was not to be considered permanent (Carlyle 2001, p.502). According to Taylor, Purple Lake is a species of Crimson Lake with a purple cast, transparent, with great depth, and in general properties it is similar to Crimson Lake but is rather more durable. The same author also describes Indian Purple, prepared by precipitating the colouring matter of a decoction of cochineal on a base of oxide of copper: a very deep-toned but rather cold and subdued purple, apt to blacken under ordinary conditions of exposure. (Taylor, n.d., pp.59-60)

Regarding the durability of cochineal pigments, in general, they were not considered permanent to light and authors did not recommend their use: “Beautiful and rich as are the colours prepared from cochineal, not one of them should ever find a place upon the palette of the artist. It is not necessary to say more about the various cochineal pigments, nor to point out their many falsifications, for their value as artists’ colours is very small. No artist who cares for his work and hopes for its permanency should employ them.” (Church 1915, pp.208,209). Even the finest of cochineal colours, carmine, was considered fugitive by some authors (Field 1835, p.45; Schweppe and Roosen-Runge 1986; Hurst 1892, p.254; Mayer 1991, p.41). Mérimée referred that “carmine is seldom used in oil painting, except by those who paint flowers. It is a brilliant colour, but it does not long resist the action of a strong light” (Mérimée 1839, pp.116,117). In turn, Salter remarked: “Although not to be classed as durable,...carmine is more stable than the weaker crimson, scarlet and purple lakes.” (Carlyle 2001, p.507 citing Salter 1869, 134).

Underlining the particularity of cochineal pigments, later, in the twentieth century, Harrison wrote that they “are only made successfully by very few manufacturers, there are no synthetic dye lakes which quite take their place. There are not more than one or two firms in England and three or four in France who still make satisfactory cochineal lakes. The processes are very round-about and complicated, numerous ingredients being used apparently without any definite logical explanation, but all apparently essential.” (Harrison 1957, pp.246,247).

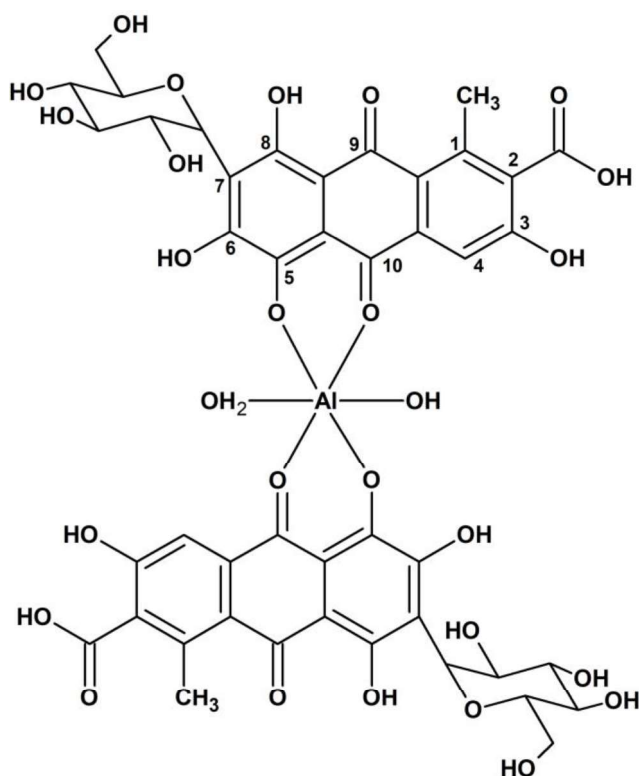


**Figure 10.** Possible structure for cochineal lake pigments based on Favaro et al. 2002.

aluminium atom coordinated to two carminic acid ligands through the 10-carbonyl group and the adjacent phenolate (5,10 coordination), forming a six-membered chelate ring structure, **Figure 10**.

Another challenging characteristic associated with cochineal pigments is that their exact molecular structures are not known yet. Some possibilities have been proposed but, to the best of the author's knowledge, no confirmation has been obtained through experimental evidence based on accurate references (Meloan, Valentine, and Puchtler 1971; Favaro et al. 2002; Dapson 2007; Harris et al. 2009; Sabnis 2010, p.88; Kunkely and Vogler 2011; Šuleková et al. 2017). These proposals are influenced by the studies on the molecular structures of alizarin complexes which culminated in the work of Kiel and Heertjes (Kiel and Heertjes 1963a, 1963b). One example of the molecular structure presented for cochineal pigments describes an



## Chapter 2

# Winsor & Newton's Cochineal Products

This second chapter starts with a summary of the history of Winsor & Newton and the development of their nineteenth century archive database. It is followed by a sub-chapter that focuses on the assessment of the content of the database with respect to W&N's cochineal products - Carmine, Crimson Lake, Scarlet Lake and Purple Lake - showing the importance of cochineal materials within W&N's pigment production, and on the selection of the most representative manufacturing processes.

Part of this chapter resulted in an oral communication and a conference proceeding of the ICOM-CC 18th Triennial Conference, Copenhagen, 4-8 September 2017 (Vitorino et al. 2017).

### 2.1. Winsor & Newton and their 19th Century Archive Database

The present section of this thesis owes much to the work of Vanessa Otero, the first author to fully explore the Winsor & Newton 19th Century Archive Database. In her doctoral thesis, Otero presents the context of 19th century colourmen and the history of Winsor & Newton,<sup>17</sup> demonstrates how the Winsor & Newton Archive reveals that they were committed to producing high quality products, and introduces the Archive Database, detailing its contents, advantages and limitations (Otero 2018).

To understand the relevance of Winsor & Newton and their 19th century archive database, it is

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<sup>17</sup> Regarding the history of Winsor & Newton, the reader is also referred to Don Pavey and Peter Staples' *The Artists' Colourmen's Story*, published in 1984.

important to have a glimpse of the context in which they appeared. As previously stated, the nineteenth century was the period of rise and proliferation of artists' colourmen. With many choices and sources of supply (see, for example, Simon 2019), the contemporary artists were forced to rely on these artists' manufacturers and suppliers, which left them vulnerable to deceits (Bomford et al. 1990, pp.51-55; Carlyle 2001, p.4). Indeed, throughout the century, complains were made about the quality of artists' colours and colourmen were accused of being more worried with profits than with quality (Bomford et al. 1990, pp.32-37). Artists were concerned that labels would provide inaccurate information regarding the material's composition, i.e. that deliberate falsification of pigments and use of poor quality materials was taking place (Clarke 2009). Clarke 2009 citing Carlyle 1993 and Townsend et al. 1995 has confirmed that adulteration and substitution of permanent materials by less permanent and cheaper ones was occurring. For example, cheaper impermanent brazilwood lake pigments were sometimes added to madder lake pigments (Bomford et al. 1990, pp.32-37). Pyle and Pearce's own words translate well the panorama: "Early in the nineteenth century, the reliability of artists' colours was inconsistent and questionable. Until Winsor & Newton." (Pyle and Pearce 2001, p.5).

Winsor & Newton was founded in 1832 by William Winsor (1804-1865) and Henry Charles Newton (1805-1882), **Figure 11**, at No. 38, Rathbone Place, London, as an artists' colourman's shop close to already well established artists' colourmen such as George Rowney & Co. and Reeves & Sons (Otero 2018, p.8 and references cited therein). Henry Newton was a painter, while William Winsor, a colour chemist and artist, brought to the partnership the scientific knowledge that had been missing from the artists' colourmen trade and which was to guarantee their success (Pyle and Pearce 2001, p.5). From the start, William Winsor and Henry Newton sought to improve the quality and permanence of the pigments which were at the disposal of artists. Aware not only of the needs of the artists but also of the colourman's responsibilities, they became a regular source of reliable colours and one of the leading colourmen worldwide (Killik 1925, p.2; "Winsor & Newton - About Us" 2019). Recognition came in the form of their appointment as artists' colourmen to Queen Victoria in 1841, the first of many appointments. In the same year, Winsor & Newton extended to Nos. 37 and 39 of Rathbone Place, London, while in 1844 they expanded to Kentish Town, building a place which became known as the "North London Colour Works" (Otero 2018, p.9). World recognition begun later with the distinction of the medallion of the 1851 International Exhibition awarded for the chemistry of artists' colours (Otero 2018, p.9). Winsor and Newton's reputation spread throughout the world in the



**Figure 11.** William Winsor (left) and Henry Charles Newton (right), founders of Winsor and Newton. Figure from Fairbairn and Beal 1982, p.9.

latter part of the 1800s (Fairbairn and Beal 1982, pp.8,9).

The company worked closely with George Field (1777-1854), the most eminent English colour chemist and maker of the early nineteenth century, who specialised in the manufacture of lake pigments, especially madder, and supplied important painters such as J. W. Turner (1775-1851) and John Constable (1776-1837) (Otero 2018, p.9 and references cited therein). Aware that the trade of artists' materials was suffering from bad practice and of artists' concerns, Winsor & Newton attempted to inform and reassure customers of the quality of the materials by publishing the main ingredients of their pigments in their catalogues, including an explanation of what was meant by 'permanence' and how it was evaluated for different materials (Clarke 2008; Clarke 2009). As pointed out by Otero, Winsor & Newton was in fact the first artists' colourmen to publish the composition and permanence of their colours in 1892, however, without disclosing their manufacturing processes (Otero 2018, pp.11,31 and references cited therein).

William Winsor died in 1865 leaving his heritage to his son, William Henry Benyon Winsor (1852-1879). After Benyon's death, Henry Charles Newton purchased Winsor's share and in 1882 he sold the business to the newly incorporated Winsor & Newton Limited with shareholders from both founding families. Henry Charles Newton died a few months later, still in 1882. By the end of the nineteenth century, W&N Ltd. was fully established not only in Europe but also overseas in the United States of America, Australia and India, maintaining the quality principles laid by the founders. Winsor descendants were in the company until 1903 whereas the Newton's were until late 1970's. (Otero 2018, pp.10,11 and references cited therein)

Currently, Winsor & Newton belongs to the multinational company Swedish-based ColArt Ltd., which also detains Lefranc & Bourgeois, Reeves, Conté à Paris, Liquitex, Snazaroo and Letraset, with production facilities in the UK, France, China, India and Japan (Otero 2018, p.11 and references cited therein).

### **2.1.1. The 19th Century Archive Database**

The Winsor & Newton 19th Century Archive is a unique primary source of information on the nineteenth-century artists' materials available and their commercial preparation. Held at ColArt Fine Art & Graphics Ltd, Whitefriars Avenue, Harrow, Middlesex, England, the archive includes hand-written recipes books, account books and catalogues, as well as miscellaneous details of W&N's work from the beginning of their company through to the twentieth century (Clarke and Carlyle 2006; "Winsor & Newton Archive" 2019; "Winsor & Newton Archive of 19th Century Artists' Materials" 2019). It covers detailed information on the manufacture of pigments, grounds, binders, mediums, varnishes and the preparation of oil tube paints and watercolours, thereby providing an invaluable insight into 19th century artists' materials along with factory-floor practices of a major 19th century artists' manufacturer. As far as it is known, it is the most extensive and detailed historical archive of nineteenth century colourmen ("Winsor & Newton Archive" 2019). Using Otero's own words, "Access to these records gives a rare insight into W&N's true concern for the quality, durability and reliability of their products." (Otero 2018, p.27). The recipes books contain dated records of the precise

composition of a production or experimental batch, which sometimes are numbered, commonly accompanied by comments on the effectiveness of the batch. Working notes accompanying recipes show how - and when - processes were made and revised to improve quality, reduce expenses, or take account of variability in raw materials. Moreover, sometimes pieces of paper were painted with the products of the batch and pasted in (e.g. book 7P page 304, book A4 page 035B, book P2 page 332A, and several pages in book A6). The range and amount of information contained within these books allows to determine what materials were used to create a given pigment, colour mixture, or tube paint, which is essential information for interpreting analytical data from actual artworks. As stated by Clarke and Carlyle 2006, to establish whether an artist mixed a given set of pigments to achieve a colour, or added certain materials to their paint, or whether this was done by the colourman is significant in understanding the artists' choices and individual relationship to their materials.

In order to make the Winsor & Newton 19th Century Archive accessible, a page-image database was compiled combining photographs of each page of the nineteenth hand-written books and catalogues with an indexing system containing information about their content (Clarke and Carlyle 2005a; Clarke and Carlyle 2005b). This combined database was built during a four-year project which begun in 2004 by a team led by Leslie Carlyle and Mark Clarke working in England and the Netherlands, and in collaboration with Winsor & Newton (Clarke 2008; Clarke 2009).<sup>18</sup> It has been available since 2006.

The figure displays a screenshot of a digital database interface for the Winsor & Newton 19th Century Recipe Database, alongside a scanned image of a handwritten recipe page from a book.

**Database Record (Left):**

- Recipe Name:** Damp Lake
- Recipe Name Interpreted:** damp lake
- Restriction:** unrestricted
- Book:** 08
- First Page:** P042
- First Line:** 01
- Unique Recipe Code:** 08P042L01
- Topic:** pigment manufacture
- Sub Topic:** damp lake
- Ingredients Table:**

| materials: original name | materials: interpreted name      | qualifier | units  | quantity | SI units  |
|--------------------------|----------------------------------|-----------|--------|----------|-----------|
| Carb Ammo                | ammonium carbonate               |           | pound  | 2        | 907 kg    |
| aq                       | water                            | hot       | gallon | 2        | 9.1 litre |
| Aq                       | water                            | cold      | gallon | 2        | 9.1 litre |
| aqua                     | water                            |           | gallon | 250      | 1137.5    |
| Al                       | alum                             |           | pound  | 5        | 2.268     |
| W&N Liquor               | [unclear, cochineal lake liquor] |           | gallon | 2        | 9.1 litre |
- Search Fields:** Carb Ammo, ammonium carbonate
- Equipment Materials:** date: 05 12 1946, disposes durability: yes/no, illustration: yes/no, specifies costs or prices: costs/prices, disposes quality: yes/no, sample attached: yes/no, marginal numbering, named individuals and companies

**Handwritten Page (Right):**

The handwritten page contains a recipe for 'Damp Lake' in cursive script. The text is as follows:

Damp Lake. Small batch. Not 23 Feb  
 2<sup>nd</sup> Carb Ammo. dissolved in a solution of  
 2 Gallons hot & 2 Gallons cold Aq. put into  
 250 Gallons Aq.  
 5<sup>th</sup> Feb. 21. Added in as usual.  
 add  
 2 Gallons White Lead. 25 to 50  
 (Ordinary 11<sup>th</sup> or 12<sup>th</sup> 10<sup>th</sup> to 15<sup>th</sup> to 20<sup>th</sup>  
 make a fair cheap common lake.  
 Gamboge dissolved in Carb Soda by boiling in  
 water. then evaporated to dryness is  
 soluble by standing in spirit of wine.  
 The soda is here dissolved in a caustic state  
 this wine is confirmed by the appearance  
 dissolves while the solution in carb soda  
 is taking place. the Gamboge performs the part  
 of an acid to the soda.  
 This solution of Gamboge in spirit of wine with  
 heavy solution with water without the resin  
 being thrown down.  
 Perhaps it need not be evaporated, but the  
 spirit put into the aqueous solution & in

**Figure 12.** Example of a database window: database record for a Damp Lake record (URC 08P042L01) (left) and the corresponding page-image (right). Figure from the "Winsor & Newton Archive of 19th Century Artists' Materials" 2019.

<sup>18</sup> The project was initiated by Leslie Carlyle and undertaken with Mark Clarke. It was originally begun as a pilot project within the 'De Mayerne Programme' (2002-2006) which was funded by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) from 2003 to 2005. The database resulting from the pilot project, named the Researcher's Edition (RE) is currently hosted in five locations, see note below. Work to expand and add detail to the Researcher's Edition was continued under the direction of Mark Clarke. This work took place thanks to Ian McClure's kind reception for it, at the Hamilton Kerr Institute, and was funded by the Arts and Humanities Research Council (AHRC) from 2006 to 2008 (Otero 2018, p.27 and references cited therein).

The page-image database, **Figure 12**, displays full-page high-resolution colour digital images of the original books' pages and allows to zoom into the image, navigate around it, adjust the brightness and contrast, as well as to move pages forward and back within a given book. The contents of the archive are thus available without requiring exhaustive transcription or complex editing, allowing researchers easy, fast and flexible access to the archive, avoiding the need for visiting it, and most importantly handling such rare manuscripts (Otero 2018, p.27 citing Clarke and Carlyle 2005a and Clarke and Carlyle 2005b).

The index database with text-based summary fields of contents for each individual record is displayed alongside. The index includes the original name of the record and an interpreted name (the subject or title of the recipe expressed in modern terminology), the topics and sub-topics associated with it, a list with the materials as they appear in the record, together with interpretations using modern terminology, qualifiers and quantities used (original British units and SI international units). Other fields include the date of the record, equipment, and any named individuals or companies. The manuscripts may be examined page-by-page or by directly accessing a page that contains a recipe identified during a search of the index database (Clarke 2008). A term can be searched anywhere in the database by using the All Fields search option. It is also possible to restrict the search, such as searching recipes within a date range. Individual Fields can be searched as well, one or more at a time, such as the original title of the recipe or the recipe name interpreted, topics, sub-topics, or an ingredient in its original or modern terminology (Otero 2018, p.30).

Further information regarding the database can be found in Otero 2018 and in "Winsor & Newton Archive of 19th Century Artists' Materials" 2019. Despite being an invaluable research tool, some inconsistencies were found while working with the database, which has been addressed by Carlyle et al. 2011 and Otero 2018. One important difficulty is the association of the database records with the topics or sub-topics. There are records with no sub-topic and records with incorrectly attributed sub-topics. There are also several records with incomplete fields.

Regarding its content, the Winsor & Newton 19th Century Archive Database combines the indexing system with digitalized page-images of 85 manuscript books (corresponding to a total of 16648 page-images) and a digital collection of 47 Winsor & Newton 19th century trade and retail catalogues covering the period between c. 1835 and 1900 (Otero 2018, pp.27,28,30). Access to the complete version of the database is only possible at ColArt Fine Art & Graphics Ltd., UK (Otero 2018, p.27). A Researcher's Edition (RE) with restricted access due to the commercial sensitivity of certain files was released at the time of its construction, which access required permission from Winsor & Newton. The Researcher's Edition is available in five locations<sup>19</sup> and contains 15003 database records with 3579 inaccessible (restricted) due to the commercial sensitivity of the

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<sup>19</sup> The Researcher's Edition of the database is available in the Netherlands, at Rijksbureau voor Kunsthistorische Documentatie (RKD); in the UK, at Department of Conservation, Tate Britain, at the Conservation and Technology Department, Courtauld Institute of Art, University of London, and at The Hamilton Kerr Institute, University of Cambridge; and in Portugal, at the Department of Conservation and Restoration, Faculty of Sciences and Technology, NOVA University of Lisbon (Carlyle et al. 2011).

information at the time the database was completed (Carlyle et al. 2011).<sup>20</sup> An online index which provides an indication of the content of the database is currently available, completely unrestricted, through which it is possible to view the first page-image corresponding to a database record ("Winsor & Newton Archive of 19th Century Artists' Materials" 2019).

Each book in the archive was assigned a 2-digit code and each page was assigned a 3-digit code. Each database record has a Unique Recipe Code (URC), which was developed by Mark Clarke, constructed by the individual book code, the page code preceded by a P (plus either A or B for recto and verso, where necessary), and the line number of the first line on the page where the recipe is found preceded by a L. The numbering of the first line of the record is necessary because there can be more than one record on a page (Otero 2018, p.28).

Research into the Winsor & Newton database started with the work of Vanessa Otero on chrome yellow pigments and has been described in a number of publications (Carlyle et al. 2011; Otero et al. 2012; Otero, Pinto, et al. 2017; Otero et al. 2017). In their publications, the authors have demonstrated the unique value of the Winsor & Newton 19th Century Archive Database for providing efficient access to records covering the commercial preparation of 19th century artists' materials.

**Table 1.** General content of the 85 handwritten books (from Otero 2018, p.32).

| Miscellaneous information | Watercolour manufacture |    |    | Pigment manufacture |    |    | Oil paint manufacture | Graining and varnish | Others* |
|---------------------------|-------------------------|----|----|---------------------|----|----|-----------------------|----------------------|---------|
| 01-29                     | 2C                      | C1 | M2 | 2P                  | P1 | X5 | DR                    | G1                   | ES      |
| AC                        | 2M                      | C2 | MT | 3P                  | P2 | X6 | GR                    | G2                   | LP      |
| EN                        | A1                      | C3 | WW | 4P                  | P3 | X7 | KT                    | G3                   | MA      |
| IN                        | A2                      | C4 | X1 | 7P                  | P4 | X8 |                       | V1                   | P8      |
| NA                        | A3                      | C5 | X3 | 9P                  | PM |    |                       | V2                   |         |
| OG                        | A4                      | CP | X4 | A5                  | SE |    |                       |                      |         |
| RE                        | A7                      | HS |    | A6                  | X2 |    |                       |                      |         |

\* ES stands for Estimated Costs, LP for Lead Pencil, MA for Madder and P8 concerns the preparation of spirit colours.

Otero's research work in the archive database revealed that 35 out of the 85 manuscript books indexed in the RE database, **Table 1**, consist of miscellaneous information, which can range from medical recipes to comments by chemists and colourmen and transcribed notes from chemical periodicals and patents (Otero 2018, pp.31,32). The earliest original material is found in the book entitled "A Relic of Old Times" (book RE), which is dated 1833. A collection of small books entitled "Omnium Gatherum" (books 01-29) contain various notes which extend into personal items such as medical recipes, household recipes, notes on suppliers and customers, travel and hotel suggestions, notes on buildings and services, and staff ("Winsor & Newton Archive of 19th Century Artists' Materials" 2019). There are also twenty books which primarily cover watercolour manufacture and three books covering oil paint manufacture. Restrictions are mainly found in the books concerning

<sup>20</sup> Some records were restricted which were not marked as such in the database.

watercolour and madder lake pigment manufacture (Otero 2018, p.32). Eighteen books dating from 1834 through to 1893 cover pigment manufacture. Two of these are private copies of processes belonging to the founder Henry Charles Newton (books 7P and P4) and six of them belonged to his son Arthur Henry Newton (books 4P, 9P, P1, P2, P3, X6) who worked with his father in the company. Some of the books are numbered in chronological order and, most importantly, in some books the recipes are numbered and can be tracked using these numbers in other recipes, even in a different book. A set of books on pigment manufacture with numbered recipes throughout and largely dated are labelled P1, P2, P3 and 4P. (Otero 2018, p.32)

## 2.2. Winsor & Newton's records for cochineal products

An initial and overall assessment of the content of the RE database made through its topics and sub-topics revealed that 39% of their total of 8589 database records on pigments correspond to red and purple lakes pigments (which is equivalent to 3350 database records), **Figure 13**, followed by 19% corresponding to yellow and orange pigments and 14% to brown pigments (Vitorino et al. 2017; Otero 2018, p.33). This indicates that red and purple lakes were the colours which Winsor & Newton were experimenting with the most during the 19th century. The majority of these pertain to cochineal products (59%), with the remaining lakes prepared from madder (35%), lac (2%) and other sources such as brazilwood (4%), **Figure 13**. These numbers demonstrate the importance of cochineal products within W&N's pigment production.

Evidence as to what cochineal materials were effectively available at a given time is provided in the Winsor & Newton 19th century catalogues. These were investigated by Carlyle in 2001 and more recently by Otero (Carlyle 2001, pp.502,506,507,534,535; Otero 2018, pp.35,36). According to both authors, in Winsor & Newton 19th century catalogues, the following cochineal colours were listed from their earliest catalogue (c. 1835) on: Carmine, Crimson Lake, Scarlet Lake and Purple Lake. Variations of these colours were made available throughout the century and are listed in **Table 2**, such as Burnt Carmine (from 1841 on), Ordinary Carmine (from 1863 on), Fine and Finest Orient

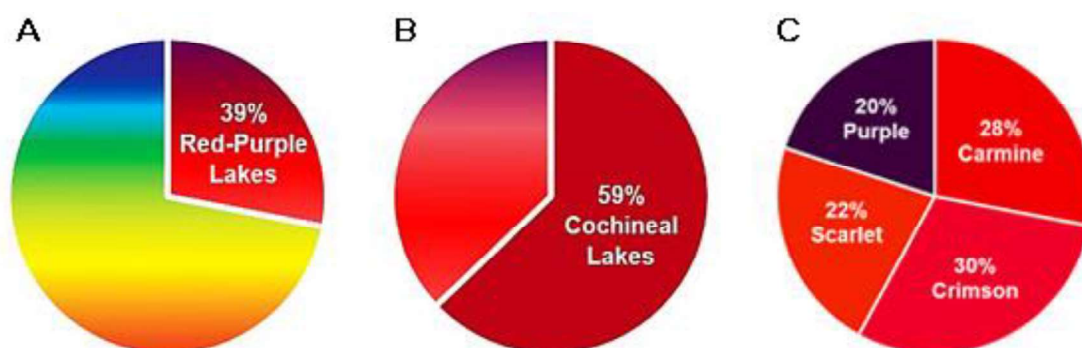


**Figure 13.** Percentage of database records for (A) red and purple lake pigments (cochineal, madder, lac, brazilwood) within the 8589 database records on pigments, and (B) cochineal lake pigments within the records for red and purple lake pigments. (C) Distribution of the production records for cochineal lake pigments within the 443 production records from 1839 to 1880 studied.

Carmine (from 1863 on), Carmine Vermilion (from 1864) and No. 2 Carmine (from 1869), Extra Crimson Lake and Indian Purple (from 1857 on). In W&N's declaration of 1892, all cochineal based lake pigments were classified as fugitive colours in water and in oil, with the exception of Burnt Carmine and Indian Purple, which were considered permanent colours. Interestingly, Scarlet Lake was listed among the permanent colours in oil (Otero 2018, p.36).

**Table 2.** Colours associated with cochineal listed in Winsor & Newton 19th century catalogues (from Carlyle 2001, pp.534,535 and Otero 2018, p.35).

| Winsor & Newton Colours |                                | Powder                   | Watercolour | Oil Colour               |
|-------------------------|--------------------------------|--------------------------|-------------|--------------------------|
| <b>Carmine*</b>         | Carmine                        | 1835 - 1887 <sup>a</sup> | 1835 - 1900 | 1835 - 1900 <sup>b</sup> |
|                         | Burnt Carmine                  | 1841 - 1900              | 1842 - 1900 | 1841 - 1900              |
|                         | Carmine, No. 2                 | -                        | -           | 1869 - 1900              |
|                         | Carmine, Ordinary              | 1863 - 1876              | -           | -                        |
|                         | Carmine, Fine                  | 1863 - 1900 <sup>c</sup> | -           | -                        |
|                         | Carmine, Finest                | -                        | -           | 1886 - 1892              |
|                         | Carmine, Finest Orient         | 1863 - 1900              | -           | -                        |
|                         | Carmine Vermilion <sup>#</sup> | 1864                     | -           | -                        |
| <b>Crimson</b>          | Crimson Lake                   | 1835 - 1900              | 1835 - 1900 | 1835 - 1900              |
|                         | Crimson Lake, Extra            | 1857 - 1900 <sup>d</sup> | -           | -                        |
| <b>Scarlet</b>          | Scarlet Lake <sup>‡</sup>      | 1835 - 1900              | 1835 - 1900 | 1835 - 1900              |
| <b>Purple</b>           | Purple Lake                    | 1835 - 1900              | 1835 - 1900 | 1835 - 1900              |
|                         | Indian Purple <sup>§</sup>     | 1857 - 1868              | 1863 - 1900 | 1886 - 1900              |

\* In p. 507, Carlyle mentions an Extra Carmine Lake listed from c.1865 to 1869 (Carlyle 2001, p.507).

<sup>#</sup> Intentional combination of carmine and vermilion (Carlyle 2001, p.507). Many shades of vermilion were available throughout the century and were distinguished by various names, such as Pale Vermilion (Carlyle 2001, p.511). A Vermilion Pale was listed in oil from 1889 on, and was not sold in powder (Carlyle 2001, p.535).

<sup>‡</sup> In their c.1896 catalogue, Winsor & Newton included the following on their Scarlet Lake: "An intimate combination of Vermilion and Alizarin Crimson. This mixture has, after careful trial, been introduced to supersede the much more fugitive compound hitherto made from Vermilion and Crimson Lake." (Carlyle 2001, p.507).

<sup>§</sup> In their c. 1896 catalogue, Winsor & Newton described Indian Purple as a copper based cochineal lake pigment for watercolours and a mixture of madder lake and French ultramarine for oil colours (Carlyle 2001, p.502).

<sup>a</sup> Carmine powder was unavailable in the catalogues from 1863 to 1876 (Otero 2018, p.35).

<sup>b</sup> Carmine oil colour was unavailable in the catalogues from 1887 to 1892 (Otero 2018, p.35).

<sup>c</sup> Carmine, Fine powder was unavailable in the catalogues from 1883 to 1887 (Otero 2018, p.35).

<sup>d</sup> Crimson Lake Extra powder was unavailable in the catalogues from 1883 to 1887 and after 1889 it was available as Crimson Lake Extra Fine (Otero 2018, p.35).

W&N's commitment to the quality of their materials and their durability, in particular to their cochineal products, is outlined in their c. 1870 catalogue: "The high standard of excellence sought by Winsor and Newton entirely set aside all common recipes and pernicious compounds, and

rendered indispensable the aid of Chemical Science. Therefore perfectly appointed Chemical Works were established by them in 1844, with steam apparatus and all the appliances auxiliary to modern Chemical Art. The advantageous results of the establishment of these Works were apparent in the production of colours totally different from those of all the other manufacturing colour houses. The old colours were improved and new ones introduced. (...) Take, for instance, the Cochineal Products, the Carmines, the Crimson, Scarlet, and Purple Lakes, wherein stability is all but secured by the elimination of acids, and those other foreign matters necessary to the primary production of the pigment, but which, if not removed, or neutralized, before the ulterior preparation of the colour, act very prejudicially to its durability.” (pp.2,3).

After the initial and overall assessment of the database records, an evaluation of all production records for cochineal materials included in the eighteen books dating from 1843 through to 1893 that cover pigment manufacture, see **Table 1**, Subchapter 2.1.1, p.24, was carried out. Following Otero’s method, a distinction has been made between the terms database record and production record. This was important since in a database record (data from the indexing system of the RE database) the corresponding archive page-image can contain more than one production record, see **Figure 12**, Subchapter 2.1.1, p.22, whereas production records (manufacturing data from the actual Winsor & Newton archive page) are not always indexed in the database. (Otero 2018, p.38) Each production record corresponds to a batch of a given product, hence different production records can correspond to a common manufacturing process. For this study, manufacturing processes were distinguished when different materials were called for, whereas small variations in proportions only were considered to belong to the same manufacturing method. Cases were also found in which the same production record involves the production of more than one batch of the same product (e.g. URC 4PP110AL01).

Four hundred and forty-three (443) production records from 1839 through 1880 were found with the main headings Carmine (28%), Crimson Lake (30%), Scarlet Lake (22%) and Purple Lake (20%), which will be described below (see **Tables 23-26**, Appendix 1, pp.113-126, for lists of all the records), **Figure 13**. Some of these headings were further modified with adjectives such as Ordinary Carmine, Fine Carmine, Finest Orient Carmine, No. 2 Carmine. However, these names given in the production records were not necessarily the names which appear for sale in Winsor & Newton’s catalogues.

The evaluation of the 443 production records for cochineal materials has resulted in the understanding that the preparation of these pigments was a matter of a big deal of experimentation (see **Table 6**, p.33 for a systematization of the records). Not only different manufacturing processes were found under the same main headings, but also small variations in proportions of ingredients were found within the same manufacturing processes. Moreover, apart from the inherent complexity of the production records for cochineal materials, one difficulty found while going through the records was the correct interpretation of some abbreviations, terms and symbols found. As explained by Clarke, some turned out to be defined within the manuscript books: “searching for abbreviations often finds the term to which they refer can sometimes be found in another separate recipe but in fully written-out form; other become obvious with increased familiarity with the material” (Clarke

2009). For example, a list of abbreviations and the respective explanations is present on page 7PF05 and notes such as that on page P1P086B referring that “A means alum & S = soda, P Verm = pale vermilion” can be found throughout the books. Other abbreviations, terms and symbols were occasionally determined from context in a particular record or records, and then generalised to other records where context alone is insufficient. Some terms were also interpreted with the support of contemporary documentary sources such as dictionaries and chemical encyclopedism of the period. A list of abbreviations gathered from cochineal records with the original term in the records and the interpreted term is presented in **Table 27**, Appendix 2, p.127.

Nevertheless, the range and amount of information contained in the investigated records and the degree of detail that they present is indeed outstanding. Most of the time, ingredients have the date and place from where they were bought; references to people and places to where Winsor & Newton would send or sell the final products can be found, as well as comparisons to materials from other manufacturers and drawings to illustrate some procedures; and the costs of the processes are frequently presented, together with comments on their effectiveness, including suggestions for improvements and doubts.

### 2.2.1. Carmine

Research for cochineal records carried out in the Winsor & Newton 19th Century Archive Database revealed that one hundred and twenty-six (126) production records correspond to Carmine, **Tables 3** and **6**.

**Table 3.** Carmine records in the 18 Winsor & Newton books dating from 1843 through to 1893 that cover pigment manufacture.

| Ingredients of the Main Manufacturing Processes             | Name of Record                       | N.º of Records | Date Range |
|-------------------------------------------------------------|--------------------------------------|----------------|------------|
| Cochineal<br>Citric acid<br>Milk<br>Sodium borate<br>Alum   | Half Orient Carmine                  | 1              | -          |
|                                                             | Orient Carmine                       | 9              | 1855       |
|                                                             | Carmine                              | 2              | 1855-1860  |
|                                                             | Fine Orient Carmine                  | 7              | 1858-1860  |
|                                                             | Finest Orient Carmine                | 43             | 1858-1872  |
| Cochineal<br>Citric acid<br>Sodium borate<br>Alum           | Carmine 2 <sup>nd</sup> Qual. Orient | 1              | 1856       |
|                                                             | Half Orient Carmine                  | 15             | 1856-1858  |
|                                                             | French Carmine                       | 4              | 1880       |
| Cochineal<br>Potassium carbonate<br>Cream of tartar<br>Alum | (Fine) Printing Carmine              | 8              | 1858-1880  |
|                                                             | Lake Precipitate                     | 2              | 1858-1872  |
|                                                             | Ruby Carmine                         | 15             | 1869-1872  |
|                                                             | Carmine                              | 7              | 1861-1872  |
|                                                             | Extra Ruby Carmine                   | 3              | 1873       |
|                                                             | Carnation                            | 9              | 1868-1879  |

The main manufacturing process, i.e. the one carried out the most, appeared under the heading “Finest Orient Carmine” (designated in this work as FOC). It was also found under other names such as “Orient Carmine” and “Fine Orient Carmine”. Sixty-two records were found, dated from 1855 to 1872. In this main process, colour was extracted from ground cochineal insects<sup>21</sup> in an acid solution formed by the addition of citric acid,  $C_6H_8O_7 \cdot H_2O$  (throughout the records, Winsor & Newton used abbreviations for citric acid such as Cit Ac and CA). New milk (abbreviated by Winsor & Newton to N W), a source of calcium ions, taken directly from the cow, was then added. The solution was filtered and then potash alum,  $AlK(SO_4)_2 \cdot 12H_2O$  (A or Al) and borax,  $Na_2B_4O_7 \cdot 10H_2O$  (B S or Bor Soda) were added. The main proportion between ingredients found within this process was 1.0 / 0.063 / 3.2 / 0.125 / 0.063 (cochineal / citric acid / milk / borax / alum). A variation of this main manufacturing process without the addition of milk was found in twenty records under the heading “Half Orient Carmine” (code HOC). The main proportion between ingredients found in this case was 1.0 / 0.063 / 0.125 / 0.063 (cochineal / citric acid / sodium borate / alum).

The remaining forty-four carmine records dated from 1858 to 1880 were mainly headed “Ruby Carmine” (code RyC), “(Fine) Printing Carmine” and “Carmine”. In this process, extraction of colour from the cochineal insects was carried out in alkaline environment with sub carbonate of potash,  $K_2CO_3$  (abbreviated to Sub C P, S C P, Sub Carb Potassa or Potassa Carbonate) followed by the addition of alum. Cream of tartar,  $KC_4H_5O_6$  (Bi Tartrate Potash, Bi T P, Cr Tart or C T) was then added. The main proportion between ingredients found within this manufacturing process was 1.0 / 0.063 / 0.125 / 0.250 (cochineal / alum / potassium carbonate / cream of tartar). Winsor & Newton experimented with this process further to produce their crimson and scarlet products mentioned below.

It is curious to note the general absence of tin from the Winsor & Newton manufacturing processes for cochineal lake pigments, particularly, carmines. Tin is described in the literature as a complexing ion commonly associated with cochineal lake pigments from the seventeenth century onwards, used to produce distinctive red hues (Bommel, Geldof, and Hendriks 2005; Kirby, van Bommel, and Verhecken 2014), and it is known that it was employed by Winsor & Newton for their brazilwood lake pigments (Vitorino et al. 2016). According to Bommel, Geldof, and Hendriks 2005, the aluminium/calcium-based cochineal lakes appear to be much more stable than the tin-based ones, which may be one possible explanation for the absence of this ingredient in the Winsor & Newton manufacturing processes for cochineal products. Not only that, according to Carlyle 1993, carmine was reported to have frequently been adulterated with starch, a cheaper material, which was also not found in W&N’s carmine records. This evidences W&N’s commitment to the quality of their cochineal materials and their durability.

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<sup>21</sup> Different varieties of cochineal are mentioned throughout the records, such as shelly black cochineal, Honduras silver cochineal, Teneriffe cochineal and Mexican cochineal. A note found on pages P1P098B and P1P099B refers that “Teneriffe black cochineal produced a good liquor strong & bright, the same process & proportions answer for the boiling. This is a convenience because good Teneriffe can almost always be obtained whereas Mexican is very uncertain. Teneriffe might make a good carmine.”. On page P1P186B, it is also possible to read: “We have used Honduras silver cochineal to make lake precipitated with, & as the silver was estimated to be weaker than the black we took 7 lbs of this silver cochineal instead of 6 lbs keeping the other materials the same.”.

### 2.2.2. Crimson and Scarlet Lakes

Research for cochineal records carried out in the Winsor & Newton 19th Century Archive Database revealed that one hundred and thirty-two (132) production records dated from 1839 to 1879 correspond to Crimson Lake products, and that ninety-six (96) records from 1843 to 1880 correspond to Scarlet Lake products, **Tables 4-6**.

**Table 4.** Crimson records in the 18 Winsor & Newton books dating from 1843 through to 1893 that cover pigment manufacture.

| Ingredients of the Main Manufacturing Processes                | Name of Record             | N.º of Records | Date Range |
|----------------------------------------------------------------|----------------------------|----------------|------------|
| Lake pigment dispersion*<br>Alum<br>Ash                        | Crimson Lake               | 9              | 1839-1847  |
|                                                                | Extra N° 1 Crimson Lake    | 6              | 1843-1847  |
|                                                                | Extra Fine Crimson Lake    | 1              | -          |
| Lake pigment dispersion*<br>Alum<br>Sodium carbonate           | Crimson Lake               | 7              | 1847-1850  |
|                                                                | Extra N° 1 Crimson Lake    | 6              | 1847-1851  |
|                                                                | Extra Strong Crimson Lake  | 5              | 1853-1854  |
|                                                                | Fine Crimson Lake          | 2              | -          |
| Lake pigment dispersion*<br>Alum<br>Ammonium carbonate         | (Extra) Crimson Lake       | 39             | 1851-1872  |
|                                                                | Damp Crimson Lake          | 5              | 1870-1879  |
|                                                                | Extra N° 1 Crimson Lake    | 6              | 1848-1850  |
|                                                                | (Extra) Fine Crimson Lake  | 16             | 1846-1872  |
| Lake pigment dispersion*<br>Alum<br>Ash<br>Starch              | Crimson Lake               | 11             | 1843-1847  |
|                                                                | Common Crimson Lake        | 1              | 1845       |
|                                                                | Extra Crimson Lake         | 2              | 1846       |
| Lake pigment dispersion*<br>Alum<br>Sodium carbonate<br>Starch | Crimson Lake               | 2              | -          |
| Lake pigment dispersion*<br>Plaster of Paris                   | Rough Crimson Lake         | 3              | 1855-1866  |
|                                                                | Crimson Lake for Oil       | 6              | 1869-1879  |
|                                                                | Rough Crimson Lake for Oil | 5              | 1856       |

\* The lake pigment dispersion was obtained by dispersing the lake pigment produced from the alkaline extraction manufacturing process (cochineal, potassium carbonate, cream of tartar and alum) with water or ammonia.

The crimson products were characterised by the presence of an aluminate or extender (designated in W&N's records as body). The aluminate was composed of alum and an alkaline compound. This was added to a lake pigment dispersion (designated in W&N's records as "Lake Precipitate Liquor", "Lake Precipitate", "Lake Liquor" or "Boiling") which resulted from the "Ruby

Carmine” manufacturing process previously described.<sup>22</sup> W&N’s experimentation was mainly related to the alkaline compounds of the aluminate and included the use of ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ) designated as Carb Ammo, C A or Amm Carb (66 records dated from 1846 to 1879), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) designated as Soda, S or Carb Soda (20 records, dated from 1847 to 1854), and ash (16 records dated from 1839 to 1847). Two particular types of aluminate composed of ash and starch (14 records dated from 1843 to 1847) and of sodium carbonate and starch (2 records without date) were also experimented with. These production records were found under several headings, for example, “Fine Crimson”, “Extra N° 1 Crimson”, and “Damp Crimson”.

It is interesting to note that Winsor & Newton used ash and starch only up until 1847. After that date, these ingredients no longer appear. According to Bommel, Geldof, and Hendriks 2005, starch is sometimes known to have been used as a substrate for the organic red pigments, or as an inert additive to obtain a lighter shade of red lake. It could also be added as a cheap extender during grinding of the pigment, or already during precipitation of the lake to give the paint more body (Bommel, Geldof, and Hendriks 2005).

A further manufacturing process was characterised by the addition of the extender plaster of Paris<sup>23</sup> (14 records dated from 1855 to 1879) instead of the aluminate. This is the only crimson lake product where apparently calcium ions were present. These production records were mostly headed “Rough Crimson” and “Crimson Lake for Oil”.

For the Scarlet Lake products, the same manufacturing pathway as for Crimson Lakes was used, with the same lake pigment dispersion and aluminate. The difference was that pale vermillion, HgS (designated in W&N’s records as P V or P Verm) was consistently added. The most common aluminate for scarlet was made of alum and ammonium carbonate (40 records dated from 1847 to 1879). A considerable number of aluminates were also made of alum and sodium carbonate (36 records dated from 1847 to 1880). Records for scarlet lakes which bodies included ash (4 records dated from 1843 to 1846), ash plus starch (8 records dated from 1843 to 1844) and ammonium carbonate plus sodium carbonate (8 records dated from 1851 to 1853) were also found. These production records were mainly headed “Marbler’s Scarlet”, “Fine Scarlet”, and “LM Scarlet”.

### 2.2.3. Purple Lake

Research for cochineal records carried out in the Winsor & Newton 19th Century Archive Database revealed that eighty-nine (89) records correspond to Purple Lake products. The purple lake manufacturing records showed a complex procedure with no consistent manufacturing

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<sup>22</sup> Some crimson records detail all the steps of the manufacturing process to produce the lake precipitate liquor following the alkaline extraction (e.g. URC X5P048AL01 and P3P079AL01), whereas most of the crimson records simply refer to other records that describe the full process (e.g. URC 7PP022L01 and P1P135AL16).

<sup>23</sup> Plaster of Paris is made by calcining gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) at temperatures of a minimum of 90 °C, but usually to temperatures of 150-165 °C to produce hydrates with the formula  $\text{CaSO}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  which are then reconstituted by slaking with water and then curing (drying) to re-form gypsum (Eastaugh et al. 2004, p.300-301 citing Bezou et al. 1995 and Manning, 1995, p.155).

processes found, which did not allow for a systematization of the processes as was carried out for the carmine, crimson and scarlet (see **Table 6**). Each purple production record concerns a different process carried out with cochineal insects or, generally, with supernatant solutions that had already been used for the Carmine, Crimson Lake and Scarlet Lake pigments. For example, on URC P1P097AL01 (Double Lake Liquor) it is referred that “(...) the grouts [cochineal dregs] that remain behind have certainly a little colouring matter left in them, but of a poor character. These grouts are put by for boiling for purple lakes.”.

Most of the purple lake pigments were however characterised by the addition of sulphate of zinc ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) together with alum to the referred supernatant solutions. These were headed under various names such as “Light Purple Lake”, “Purple Lake No. 63”, and “Deep Purple Lake”. A particular type of purple lake made with sulphate of copper and sulphate of iron instead of sulphate of zinc was also found under the heading “Indian Purple” (7 records dated from 1853 to 1872).

**Table 5.** Scarlet records in the 18 Winsor & Newton books dating from 1843 through to 1893 that cover pigment manufacture.

| Ingredients of the Main Manufacturing Processes                                         | Name of Record               | N.º of Records | Date Range |
|-----------------------------------------------------------------------------------------|------------------------------|----------------|------------|
| Lake pigment dispersion*<br>Alum<br>Vermilion<br>Ash                                    | Scarlet Lake                 | 1              | 1843-1846  |
|                                                                                         | Scarlet Lake N° xxx          | 3              |            |
| Lake pigment dispersion*<br>Alum<br>Vermilion<br>Sodium carbonate                       | Scarlet Lake                 | 8              | 1848-1879  |
|                                                                                         | Fine Scarlet Lake            | 12             | 1847-1855  |
|                                                                                         | Carriage Lake                | 3              | 1877-1880  |
|                                                                                         | Marbler's Scarlet Lake       | 4              | 1848-1850  |
|                                                                                         | Extra Marbler's Scarlet Lake | 4              | 1850       |
|                                                                                         | Damp Scarlet Lake            | 5              | 1872-1873  |
| Lake pigment dispersion*<br>Alum<br>Vermilion<br>Ammonium carbonate                     | (Extra) Scarlet Lake         | 14             | 1864-1871  |
|                                                                                         | (Extra) Fine Scarlet Lake    | 10             | 1847-1879  |
|                                                                                         | Marbler's Scarlet Lake       | 4              | 1859-1863  |
|                                                                                         | Marbler's Scarlet Lake N° 2  | 1              | 1869       |
|                                                                                         | Damp Scarlet Lake            | 11             | 1856-1871  |
| Lake pigment dispersion*<br>Alum<br>Vermilion<br>Ash<br>Starch                          | Scarlet Lake                 | 5              | 1843-1844  |
|                                                                                         | Scarlet Lake for Tubes       | 3              |            |
| Lake pigment dispersion*<br>Alum<br>Vermilion<br>Ammonium carbonate<br>Sodium carbonate | Fine Scarlet Lake            | 6              | 1851-1853  |
|                                                                                         | Extra Fine Scarlet Lake      | 2              |            |

\* The lake pigment dispersion was obtained by dispersing the lake pigment produced from the alkaline extraction manufacturing process (cochineal, potassium carbonate, cream of tartar and alum) with water or ammonia.

**Table 6.** Number of records, ingredients and manufacturing processes for W&N's Carmine, Crimson Lake and Scarlet Lake.

| Cochineal                                                                         |                                                                                   | Extraction Method                                                                   |                                                                                     | Complexing agent                                                                    |                                                                                     | Additives                                                                            |                                                                                       |                                                                                     |
|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Carminic acid                                                                     | Citric acid                                                                       | Potassium carbonate                                                                 | Alum (Al <sup>3+</sup> )                                                            | Milk                                                                                | Sodium borate                                                                       | Cream of tartar                                                                      |                                                                                       |                                                                                     |
|  |  |    |    |   |  |   |                                                                                       |                                                                                     |
| Aluminate/Extenders                                                               |                                                                                   |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                      |                                                                                       |                                                                                     |
| Ammonium carbonate + Alum                                                         | Sodium carbonate + Alum                                                           | Ash + Alum                                                                          | Starch                                                                              | Plaster of Paris                                                                    | Vermilion                                                                           |                                                                                      |                                                                                       |                                                                                     |
|  |  |    |    |  |  |                                                                                      |                                                                                       |                                                                                     |
| Production Name                                                                   | # of Records                                                                      | Manufacturing Process                                                               |                                                                                     |                                                                                     |                                                                                     |                                                                                      |                                                                                       |                                                                                     |
| Finest Orient Carmine                                                             | 62                                                                                |    |    |    |    |    |    |  |
| Half Orient Carmine                                                               | 20                                                                                |   |   |   |   |   |                                                                                       |                                                                                     |
| Ruby Carmine                                                                      | 44                                                                                |  |  |  |  |  |  |                                                                                     |
| Production Name                                                                   | # of Records                                                                      | Manufacturing Process                                                               |                                                                                     |                                                                                     |                                                                                     |                                                                                      | # of Records                                                                          | Production Name                                                                     |
| Crimson                                                                           | 66                                                                                |  |  |  |  |  | 40                                                                                    | Scarlet                                                                             |
|                                                                                   | 20                                                                                |  |  |  |  |  | 36                                                                                    |                                                                                     |
|                                                                                   | 16                                                                                |  |  |  |  |  | 4                                                                                     |                                                                                     |
|                                                                                   | 14                                                                                |  |  |  |  |   | 8                                                                                     |                                                                                     |
|                                                                                   | 14                                                                                |  |  |  |                                                                                     |                                                                                      |                                                                                       |                                                                                     |
|                                                                                   | 2                                                                                 |  |  |  |  |                                                                                      |                                                                                       |                                                                                     |
|                                                                                   |                                                                                   |  |  |  |  |   |   | 8                                                                                   |

\* LPD = Lake pigment dispersion obtained by dispersing the lake pigment produced from the alkaline extraction manufacturing process with water or ammonia.



## Chapter 3

# Reconstruction and Characterisation of Cochineal Lake Pigments

This third chapter starts with the characterisation of carminic acid in solution using absorption and fluorescence spectroscopies. It is followed by a sub-chapter that presents the reconstruction and characterisation with a multi-analytical approach of the most representative manufacturing processes of W&N's cochineal products (Carmine, Crimson Lake, Scarlet Lake and Purple Lake) and the validation of historically accurate reference materials, whenever possible, through comparison with historical samples of cochineal pigments and tubes of oil paint from Winsor & Newton. The multi-analytical approach included ICP-AES,  $\mu$ EDXRF, FORS,  $\mu$ Raman,  $\mu$ FTIR, SERS ( $\lambda_{exc} = 633$  nm) and  $\mu$ spectrofluorimetry.

Part of this chapter resulted in a poster presentation at the 4th International Congress Chemistry for Cultural Heritage, Brussels, 6-8 July 2016<sup>24</sup> and an oral communication at the 9th International Congress on the Application of Raman Spectroscopy in Art and Archaeology, Évora, 24-28 October 2017.<sup>25</sup>

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<sup>24</sup> Vitorino, T., Casini, A., Cucci, C., Melo, M. J., Otero, V., Parola, A. J., Picollo, M., Stefani, L. An in situ multi-analytical approach for the characterization of cochineal lake pigments. Poster presentation at the *4th International Congress Chemistry for Cultural Heritage (ChemCH 2016)*, Brussels, Belgium, 6-8 July 2016.

<sup>25</sup> Vitorino, T., Otero, V., Parola, A. J., Picollo, M., Melo, M. J. A molecular study of the 19th century Winsor & Newton cochineal lake pigments. Oral presentation at the *9th International Congress on the Application of Raman Spectroscopy in Art and Archaeology*, Évora, Portugal, 24-28 October 2017.

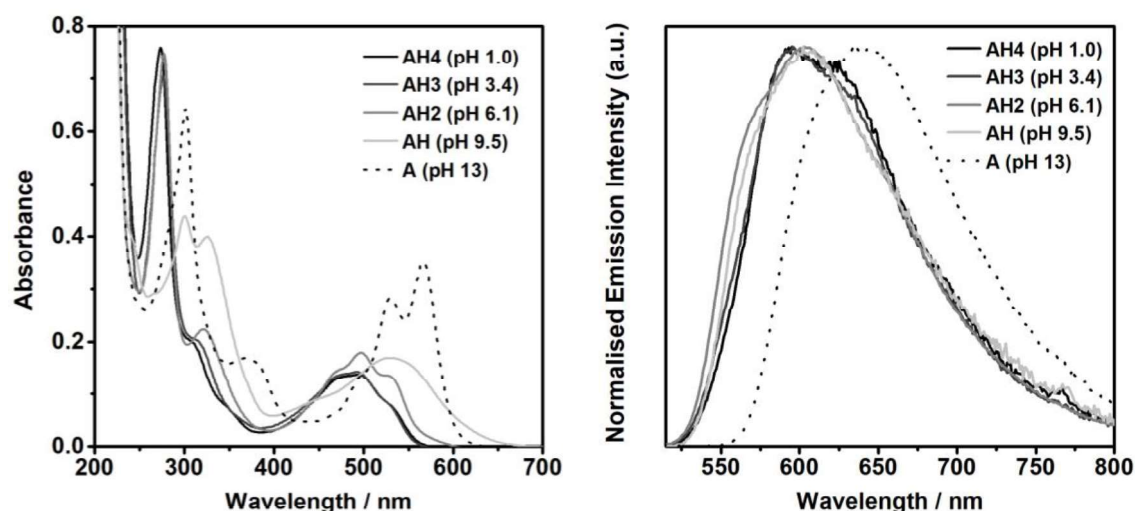


**Figure 14.** Absorption (left) and emission (right) spectra of carminic acid in aqueous solutions at various pH values.

### 3.1. Characterisation of carminic acid

In order to provide grounds for the study of cochineal lake pigments, their molecular structure and ageing, the characterisation of carminic acid in solution was carried out. Spectrophotometric and fluorimetric titrations were employed to determine the  $pK_a$  of the protolytic dissociations of carminic acid and the results obtained were compared with those presented in the literature.

The carminic acid used in this study was purchased from Sigma-Aldrich and used without further purification. A  $5 \times 10^{-5}$  M aqueous solution was used with a universal buffer and diluted HCl 1M and NaOH 5M and 1M solutions were used to raise the pH. The effect of pH on the absorption and emission spectra of carminic acid was investigated in the 1.0-13 pH range. The absorption spectra in solution were corrected to dilution. Emission spectra were obtained upon excitation at 420 nm. Further details regarding the reagents and apparatus used are presented in Appendix 3, p.128.

Five species were detected from the absorption and fluorescence spectra of carminic acid in the pH range under investigation, AH4 being the fully protonated neutral species, **Figure 14**. Each species is stable within the limited pH intervals shown in **Figure 15**. The absorption maxima of the five species shifted to the red as the pH increased, from 497 nm at pH 1 and pH 6.1 to 529 nm at pH 9.5 and to 566 nm at pH 13. The absorption spectrum at pH 6.1 presents a shoulder around 530 nm and that at pH 13 presents two well-defined absorption bands at 530 nm and 566 nm. A bathochromic shift was also observed for the emission maxima as the pH increased, from 595 nm at pH 1 to 603 nm at pH 6.1 and to 637 nm at pH 13. In both cases, the spectra of the neutral form AH4 are overlapped with those of the mono-anion AH3. The same overlap is observed for the emission spectra of species AH2 and AH. The fluorescence spectra are broad and structureless and the emission intensity increases from the fully protonated neutral species AH4 ( $4.1 \times 10^5$  cps) to the AH3 ( $9.7 \times 10^5$  cps) and AH2 ( $4.7 \times 10^6$  cps) species, where it reaches a maximum value, decreases with species AH ( $3.5 \times 10^5$  cps) reaching the minimum value, and increases again at species A ( $1.2 \times 10^6$  cps).

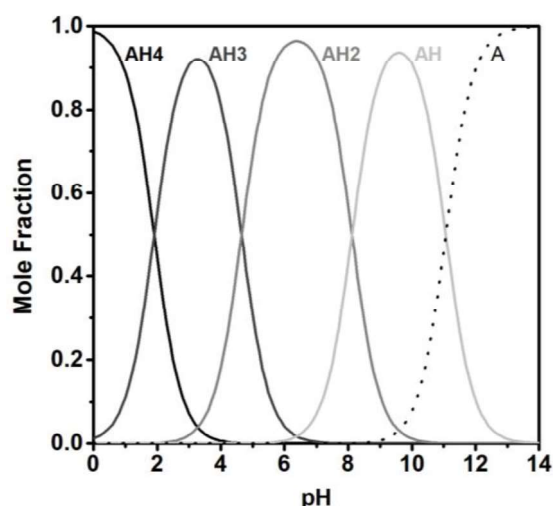


**Figure 15.** Mole fraction distribution of the five species detected from the absorption spectra of carminic acid in the 1.0 - 13 pH range.

Four dissociation constants were detected. Carminic acid is a polyprotic acid with five protons susceptible to deprotonation, at position 2 (carboxyl group) and at the phenolic groups in positions 3, 5, 6 and 8 (see **Figure 16**). The first dissociation step ( $pK_{a1} = 1.90$ ) occurs at the carboxylic group in position 2, which is the most acidic site. Favaro et al. 2002 attribute the low acidity of the carboxylic group to the “inductive electron-attracting effect of the phenolic OH group in the 3 position, which decreases the charge density in the 2 position and consequently lowers the  $pK_a$  of the COOH group”. As stated above, deprotonation at the carboxylic group does not produce appreciable

spectral changes in the molecule, where the chromatic properties are essentially determined by the hydroxyanthraquinone chromophore. With respect to the following dissociation constants obtained ( $pK_{a2} = 4.65$ ,  $pK_{a3} = 8.12$ ,  $pK_{a4} = 11.07$ ), the order of deprotonation as suggested by Favaro et al. 2002 is position 6, which is far enough away from the negatively charged site,  $COO^-$  and considering that the 5- and 8-OH groups are less acidic due to their position with respect to the carbonyl, which reduces the hydrogen mobility through hydrogen bonding, followed by positions 3 and 8, respectively, **Figure 16**. However, other authors have proposed different orders of deprotonation as presented in **Table 7**.

**Table 7.** Dissociation constants ( $pK_a$ ) of carminic acid obtained from spectrophotometric (Abs) and fluorimetric (Em) titrations and from the literature and the respective acidic centres proposed (OH).

|                                  | $pK_{a1}$ | OH <sub>1</sub> | $pK_{a2}$ | OH <sub>2</sub> | $pK_{a3}$ | OH <sub>3</sub> | $pK_{a4}$ | OH <sub>4</sub> | $pK_{a5}$ | OH <sub>5</sub> |
|----------------------------------|-----------|-----------------|-----------|-----------------|-----------|-----------------|-----------|-----------------|-----------|-----------------|
| <b>Abs</b>                       |           |                 |           |                 |           |                 |           |                 |           |                 |
| Experimental <sup>a</sup>        | 1.90      |                 | 4.65      |                 | 8.12      |                 | 11.07     |                 |           |                 |
| Favaro et al. 2002               |           | 2               | 5.47      | 6               | 8.47      | 3               | 12.10     | 8               |           | 5               |
| Jørgensen and Skibsted 1991      | 2.81      | 2               | 5.43      | 8               | 8.10      | 5               |           |                 |           |                 |
| Atabey, Sari, and Al-Obaidi 2012 | 3.39      | 2               | 5.78      | 5               | 8.35      | 6               | 10.27     | 8               | 11.51     | 3               |
| Cañamares et al. 2006            | 3.00      | 2               | 4.67      | 5               | 8.70      | 6 or 8          |           |                 |           |                 |
| Claro 2009                       | 2.90      |                 | 6.60      |                 | 10.30     |                 | 13.40     |                 |           |                 |
| <b>Em</b>                        |           |                 |           |                 |           |                 |           |                 |           |                 |
| Experimental <sup>b</sup>        | 2.44      |                 | 4.65      |                 | 8.18      |                 | 11.50     |                 |           |                 |
| Favaro et al. 2002               | 2.9       |                 | 5.31      |                 | 8.85      |                 | 12.37     |                 |           |                 |

<sup>a</sup> Dissociation constants obtained from spectrophotometric titration (using absorbances corrected to dilution).

<sup>b</sup> Dissociation constants obtained from fluorimetric titration (without correction of emission).

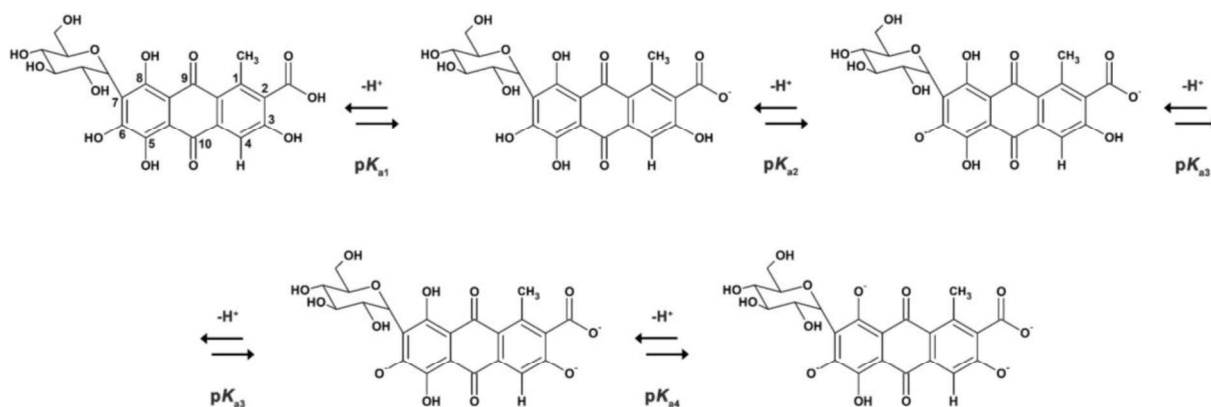


**Figure 16.** Possible acid-base equilibrium of carminic acid according to Favaro et al. 2002.

### 3.2. W&N's main manufacturing processes and experimentation for cochineal products

The preparation of historically accurate reconstructions of artists' materials using historical documentary sources supported by analyses from actual materials was initiated at the Canadian Conservation Institute and in the Netherlands as part of the MOLART programme in 1999. It continued from 2002 to 2005, as the HART Project (Historically Accurate Reconstructions Techniques), which was part of the De Mayerne Programme (Carlyle 2006; Carlyle 2012, p.33 and references cited therein; Carlyle 2018 and references cited therein). This methodology integrates the group of art technological source research, which is part of the interdisciplinary early twenty-first century field of technical art history related with the understanding of how artworks were created and with what materials (Carlyle and Witlox 2005; Nadolny et al. 2012, p.3). It has been presented in several publications such as Carlyle and Witlox 2005, Carlyle 2012a, Vitorino et al. 2016, Carlyle 2018 and Melo et al. 2018.

The shortcomings in the production of a 19th century pigment in a laboratory nowadays has been addressed by authors such as Kirby 2005 and Kirby, van Bommel, and Verheken 2014. Citing Kirby 2005, "How far is it possible to reconstruct a [late] 19th-century manufactured pigment, made on a large scale, by people with long experience of how the process should be carried out, on a small scale, by people with very little practical experience, a hundred years later?". Inevitably, the ambient conditions, the equipment, the water, chemicals and dyestuffs used are likely different. Not only that, scaling down the recipes is not necessarily a simple matter of division. The author of the present work is aware of the impossibility to reconstruct exactly the conditions under which an artists' material may have been produced in the nineteenth century. It is also known, however, that a previous author has been able to demonstrate that it was possible to obtain historically accurate reconstructions of chrome yellow pigments through the reproduction of 19th recipes from the W&N archive (Otero 2018). Following that same approach, in this work, reconstructions were prepared with as much historical accuracy as possible, referred to as historically accurate reconstructions, which are well characterised and validated as accurate references through analytical comparison



**Figure 17.** (Top) Acid extraction: cochineal solutions before and after the addition of citric acid. (Bottom) Alkaline extraction: cochineal solutions before and after the addition of potassium carbonate.

with historical artists' materials (Carlyle 2018).

After evaluation and rationalisation of the 443 records on Carmine, Crimson Lake, Scarlet Lake and Purple Lake, those considered to be the most representative, i.e. corresponding to the main manufacturing processes, were selected and reconstructed. The selection of the most representative records for reconstruction was based not only on the number of times the manufacturing process was carried out but also on the notes and comments about the batch produced, such as "capital lake when ground in oil and a nice-looking article, very lively" (book 9P page 82) and "very bright...and good strength, finest parcel yet made" (book X6 page 468). The transcription of the representative recipes used is presented in Appendix 4, pp.133-141, and the steps of the reconstructions and the respective pH values are presented in **Tables 8-10**. To carry out the reconstructions, measures from units used by Winsor & Newton were converted in modern SI units and pure chemical reagents were used, which are detailed in Appendix 3, p.128. Demineralised water (pH between 5 and 6) and glassware were also used as a starting point to control the number of variables. All precipitated pigments were washed to remove any by-products from the chemical reaction between alum and alkalis, air-dried and ground to a powder. The

characterisation of the reconstructions obtained is further detailed in Subchapter 3.2.4, pp.48-59.

To produce their Carmine, and subsequently their Crimson Lake and Scarlet Lake products, Winsor & Newton used as a basis two main manufacturing methods, which difference lies in the pH of extraction (acid or alkaline), detailed below, **Figure 17**. W&N's carmine pigments were prepared following both the acid and alkaline extraction methods, whereas their crimson lake and scarlet lake products followed only the alkaline method.

### 3.2.1. Carmine

The main manufacturing method used to produce W&N's carmines appeared under the heading *Finest Orient Carmine (FOC)* and corresponds to the acid extraction method, **Table 8**. In this process, which turned out to be very reproducible and straightforward, colour was extracted from ground cochineal insects in an acid solution formed by the addition of citric acid ( $C_6H_8O_7 \cdot H_2O$ ) which results in a red coloured solution (pH 3.8). The solution was filtrated and milk (pH around 6.7)<sup>26</sup> was then added, introducing calcium ions. The solution was filtered again and then sodium borate

<sup>26</sup> Two types of milk were experimented with: milk taken directly from the cow, which was not processed or treated, and commercial milk. The results obtained with the different milks were the same.

( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and alum ( $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) were added. In the reconstructions prepared, the pigment precipitated at a final pH around 5 with a very bright carmine colour. The supernatant solution, however, remained highly coloured as indicated in the literature (see Subchapter 1.2.2, p.15).

Analysis with infrared spectroscopy of the FOC reconstruction shows a very characteristic spectrum, **Figure 18**, believed to be a fingerprint of a complex of carminic acid with aluminium and calcium ions, which presence was confirmed by elemental analysis. Further details on these analyses are discussed below in Subchapter 3.2.4, pp.53-57. Although the molecular structure of the complex formed needs further investigation, this aluminium-calcium complex with the carminic acid has been proposed in the literature (e.g. Harris et al. 2009). This infrared spectrum also matches with an historical sample of a carmine pigment from the Winsor & Newton Archive (FOC W&N), a LeFranc tube of carmine oil paint that belonged to Amadeo de Souza Cardoso (Carmin LF), and a micro-sample of carmine paint from one of Amadeo's oil painting (see **Figure 48**, Appendix 3, pp.131,132), **Figure 18**. These findings validate the reconstruction of FOC as an accurate reference of an historical W&N carmine cochineal pigment.

Experiments of the acid extraction method were carried out without the filtration step after the addition of milk which resulted in the presence of protein in the final pigment as revealed by infrared spectroscopy, **Figure 19**. The protein is detected by the absorption bands associated with its characteristic amide group: amide I ( $\nu(\text{C}=\text{O})$  at  $1650\text{ cm}^{-1}$ ), amide II ( $\delta(\text{NH})$  and  $\nu(\text{CN})$  at  $1563\text{ cm}^{-1}$ ), and also the  $\nu(\text{NH})$  at  $3300\text{ cm}^{-1}$  (Stuart 2006). This result suggests that the filtration step after the addition of milk intended to remove the protein while keeping the calcium ions. The absence of sodium borate was also tested, resulting in some precipitation at pH around 3.5 with a slightly different infrared spectrum, **Figure 19**. This suggests that sodium borate acts as a buffer to maintain the pH of precipitation at an optimum value (slightly acidic or neutral) and that boron is present in

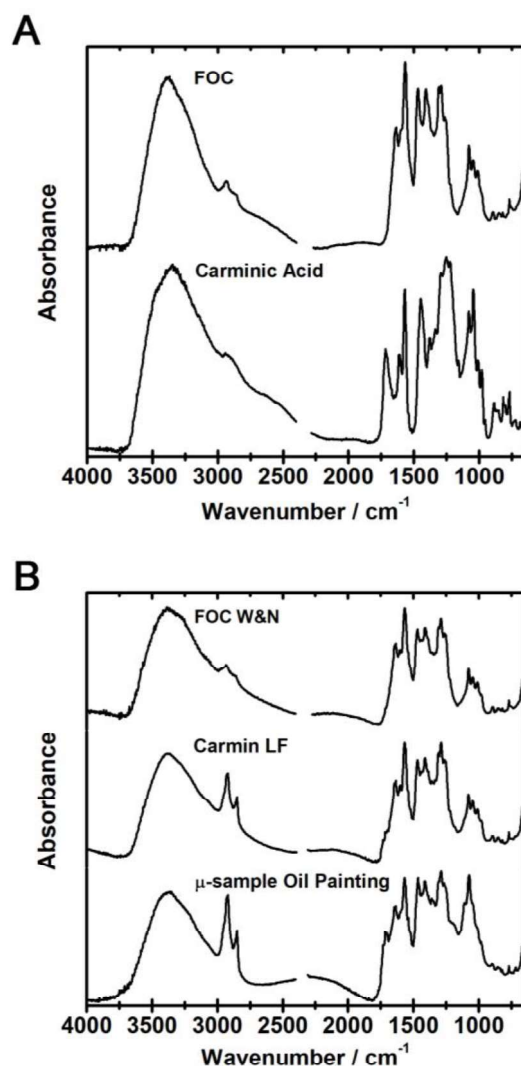


**Figure 18.** Infrared spectra of (A) carmine pigment produced from W&N's main manufacturing processes (FOC) and carminic acid and (B) carmine historical samples (FOC W&N, LeFranc tube of carmine oil paint and  $\mu$ -sample of a carmine paint from Amadeo's oil painting).

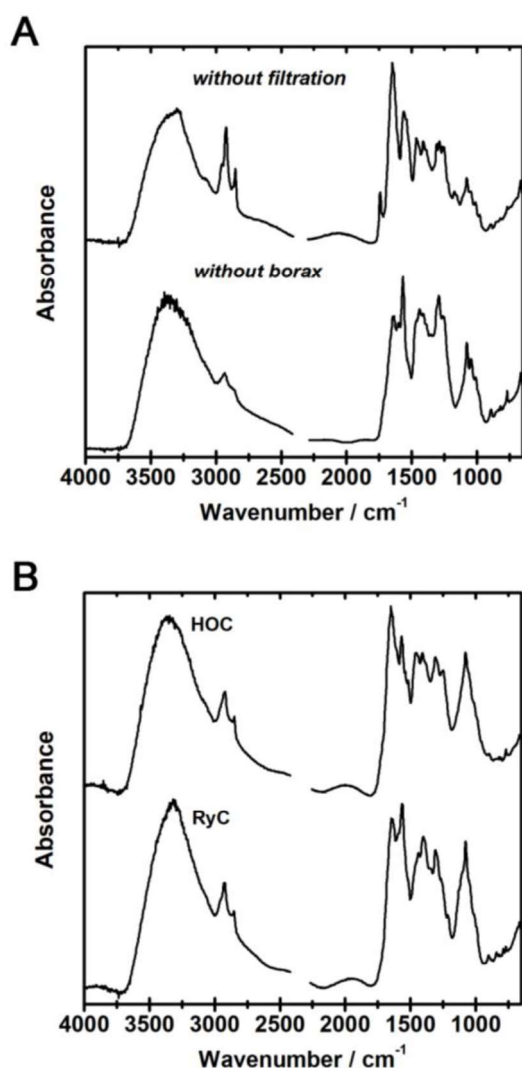


**Figure 19.** Infrared spectra of (A) the production of FOC without filtration after the addition of milk and without the addition of borax and (B) carmine pigments produced from W&N's main manufacturing processes (HOC and RyC).

Half Orient Carmine and Ruby Carmine, with infrared spectroscopy, **Figure 19**, reveals a fingerprint different from the Finest Orient Carmine and consequently a different molecular structure, which is likely explained by the absence of calcium ions.

Fortunately, and after several unsuccessful attempts to obtain an accurate reconstruction of the alkaline extraction method, the author had access to an historical sample of a W&N carmine pigment<sup>29</sup> which label identifies its production record in the Winsor & Newton 19th Century Archive

the structure of the complex formed between carminic acid and calcium.<sup>27</sup> The possible role of boron in the structure is further discussed below in Subchapter 3.2.4, pp.48-59.

A variation of this main manufacturing method was also found under the heading Half Orient Carmine (HOC) without the addition of milk, **Table 8**. In the reconstructions, the absence of milk and therefore of the calcium ions precipitates a darker red pigment at slightly lower pH values (pH 4.7), **Figure 19**. In this case too, the supernatant solution remained strongly coloured.

Winsor & Newton's second main manufacturing method, the alkaline extraction, corresponds to the Ruby Carmine (RyC), also headed Fine Printing Carmine (FPC). In this process, extraction of colour from the ground cochineal insects was carried out in an alkaline environment with potassium carbonate ( $K_2CO_3$ )<sup>28</sup> and consequently the colour of the solution obtained is more purple (pH 6.3), followed by the addition of alum and cream of tartar ( $KC_4H_5O_6$ ). In the reconstructions, precipitation occurred at a final pH around 4.20 and a dark purplish pigment was obtained, indicating that the results using the alkaline method to prepare a carmine pigment were inaccurate. Analysis of these pigments, the

<sup>27</sup> The absence of alum in the acid extraction method was also tested which resulted in no precipitation at all.

<sup>28</sup> Potassium bicarbonate ( $KHCO_3$ ), instead of potassium carbonate, was also experimented with and the results obtained were the same.

<sup>29</sup> The author is very grateful to Rebecca Pelly-Fry for access to the historical samples from the Winsor & Newton Archive Room at ColArt Fine Art & Graphics Ltd, Whitefriars Avenue, Harrow, Middlesex, England.

Database (Fine Printing Carmine, manuscript book A6, page 62). This sample was characterised with infrared spectroscopy and a spectrum similar to the Finest Orient Carmine pigments was obtained, **Figure 20**. Elemental analysis also confirmed the presence of aluminium and calcium (see Subchapter 3.2.4, p.49). However, the process referred to in the record actually corresponds to the alkaline method of extraction which does not have the addition of milk or of any other source of calcium. A closer look at the alkaline method and the materials and reagents that were used, together with a literature search, revealed that during the nineteenth century, cream of tartar (potassium hydrogen tartrate), if not pure, could contain tartrate of calcium ( $\text{CaC}_4\text{H}_4\text{O}_6$ ) in its composition (Allen 1880). To verify this hypothesis, and since no calcium tartrate or an impure sample of cream of tartar was available, the presence of calcium ions in the alkaline method was simulated by adding calcium carbonate ( $\text{CaCO}_3$ ) together with the cream of tartar, **Table 8**. The carbonate disappears, which was confirmed by the occurrence of effervescence and by the absence of the characteristic infrared absorption bands for  $\nu_{\text{as}}(\text{CO}_3^{2-})$  at  $1408\text{ cm}^{-1}$ , and for  $\delta_{\text{as}}(\text{CO}_3^{2-})$  at  $875$  and  $713\text{ cm}^{-1}$ , **Figure 20**, and the calcium ions stay as was revealed by elemental analysis (see Subchapter 3.2.4, p.49). The disappearance of the carbonate may be explained by the acid-base equilibria established by the carbonate ion.<sup>30</sup> The result was a very carmine pigment with the same infrared fingerprint of the historical sample of Fine Printing Carmine found in the archive, **Figure 20**. This validated this new reconstruction of the alkaline method and suggests that Winsor & Newton was likely using what the author now considers an impure cream of tartar, that provided the source of calcium in their process which, together with aluminium, produced a carmine product.<sup>31</sup>

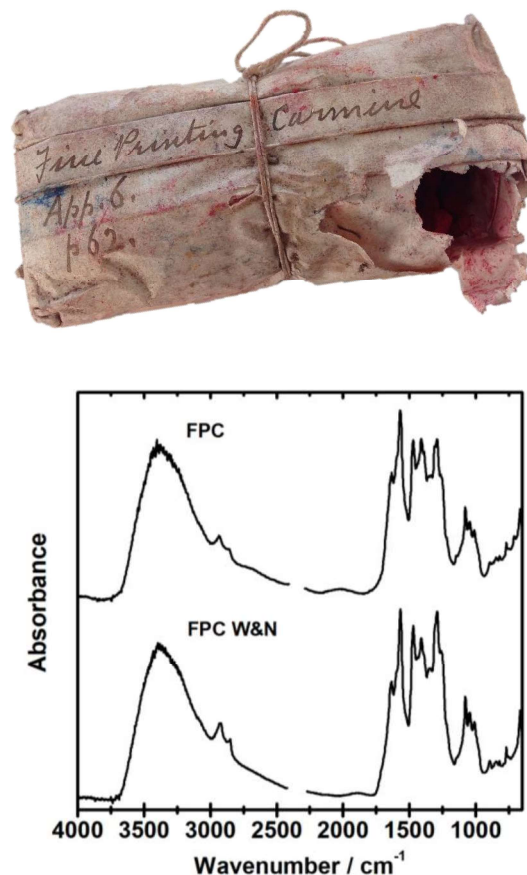


**Figure 20.** (Top) Historical sample of Fine Printing Carmine pigment from the W&N 19th Century Archive (FPC W&N). (Bottom) Infrared spectra of Fine Printing Carmine pigment produced from W&N's main manufacturing processes (FPC) and W&N Fine Printing Carmine historical sample (FPC W&N).

<sup>30</sup>  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ ;  $\text{CO}_3^{2-}(\text{aq}) + \text{H}_3\text{O}^+ \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}$  ( $\text{p}K_{\text{a}2}$  10.25);  $\text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}$  ( $\text{p}K_{\text{a}2}$  6.37);  $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O}$  (Atkins and Jones 1997, p.532).

<sup>31</sup> However, it would be important to find a sample of nineteenth century cream of tartar to confirm that it could have been the source of calcium ions in Winsor & Newton's alkaline extraction method. Although further investigation is needed, it must be noted as well that cochineal itself may also act as a source of calcium since a considerable amount of this element was detected in one of the batches of cochineal insects used during the preparation of the reconstructions, which influenced the final products obtained.

**Table 8.** Summary of the steps and pH values of the reconstructions of W&N's carmine products (transcription of the original recipes in Appendix 4, pp.133-137).

| Steps                                                                                        | pH   |
|----------------------------------------------------------------------------------------------|------|
| <b>Finest Orient Carmine</b>                                                                 |      |
| Boil 250 mL of H <sub>2</sub> O                                                              | 5.00 |
| Turn off steam                                                                               |      |
| Add 3.0 g of ground cochineal                                                                | 4.50 |
| Add 0.19 g of citric acid                                                                    | 3.80 |
| Boil 15 minutes while stirring and filtrate                                                  |      |
| Heat the filtrated solution to 84 °C and add 10 mL of fresh milk and leave one hour stirring | 4.40 |
| Filtrate                                                                                     |      |
| Boil the filtrated solution, turn off steam and keep it at 98 °C                             |      |
| Add 0.38 g of borax and stir until dissolved                                                 | 6.30 |
| Add 0.19 g of alum and leave 10 minutes stirring                                             | 5.00 |
| Centrifugate                                                                                 |      |
| <b>Half Orient Carmine</b>                                                                   |      |
| Boil 250 mL of H <sub>2</sub> O                                                              | 5.00 |
| Turn off steam                                                                               |      |
| Add 3.0 g of ground cochineal                                                                | 4.50 |
| Add 0.19 g of citric acid                                                                    | 3.80 |
| Boil 15 minutes while stirring and filtrate                                                  |      |
| Boil the filtrated solution, turn off steam and keep it at 98 °C                             |      |
| Add 0.38 g of borax and stir until dissolved                                                 | 5.60 |
| Add 0.19 g of alum and leave 10 minutes stirring                                             | 4.70 |
| Centrifugate                                                                                 |      |
| <b>Fine Printing Carmine</b>                                                                 |      |
| Boil 250 mL of H <sub>2</sub> O                                                              | 5.00 |
| Turn off steam                                                                               |      |
| Add 3.0 g of ground cochineal                                                                | 4.50 |
| Add 0.06 g of potassium carbonate                                                            | 6.30 |
| Add 0.1 g of alum                                                                            | 5.20 |
| Filtrate and leave the filtrated solution at 61 °C                                           |      |
| Add 0.06 g of alum and leave 5 minutes stirring                                              | 4.40 |
| Add 0.7 g of cream of tartar and leave 15 minutes stirring                                   | 3.40 |
| Add 0.17 g of calcium carbonate and stir <sup>a</sup>                                        | 4.20 |
| Centrifugate                                                                                 |      |

<sup>a</sup> Different quantities of calcium carbonate were experimented with. 0.17 g was the quantity which resulted in the same infrared fingerprint of the historical sample of Fine Printing Carmine found in the W&N archive.

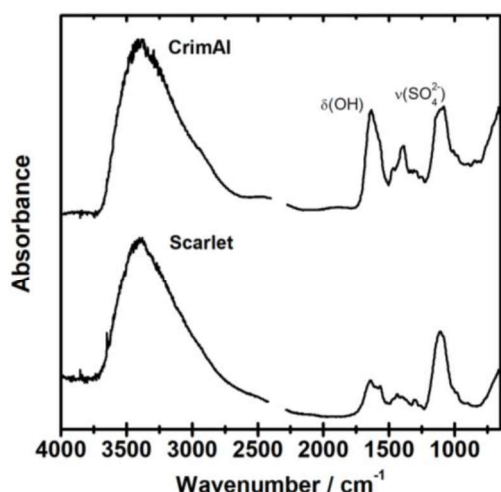


**Figure 21.** Infrared spectra of reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes (CrimAl and Scarlet).

(pH 7.5), a crimson pigment was produced at a final pH of 5.5-6 (CrimCa). A good match was achieved between the reconstruction CrimCa and an historical tube of Winsor & Newton crimson oil paint, validating the reconstruction, **Figure 22**.

### 3.2.2. Crimson and Scarlet Lakes

The crimson lakes were produced following the carmine process with alkaline extraction using potassium carbonate, **Table 9**. The carmine pigment obtained after the addition of alum, cream of tartar and calcium carbonate was dispersed with water (pH 5). To this lake pigment dispersion an aluminate composed of alum and an alkaline compound, or an extender (gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , after conversion of plaster of Paris,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) were then added. The addition of an aluminate made with ammonium carbonate (pH 5) produced a crimson pigment at a final pH of 5 (designated as CrimAl), **Figure 21**. When the aluminate was replaced by the extender gypsum

**Table 9.** Summary of the steps and pH values of the reconstructions of W&N's crimson lake and scarlet lake products (transcription of the original recipes in Appendix 4, pp.137-140).

| Steps                                                                                                          | pH   |
|----------------------------------------------------------------------------------------------------------------|------|
| <b>Rough Crimson Lake</b>                                                                                      |      |
| <i>To prepare the "lake precipitate liquor":</i>                                                               |      |
| Boil 250 mL of $\text{H}_2\text{O}$                                                                            | 5.90 |
| Turn off steam                                                                                                 |      |
| Add 3.0 g of ground cochineal                                                                                  | 5.40 |
| Add 0.06 g of potassium carbonate                                                                              | 6.21 |
| Add 0.1 g of alum                                                                                              | 5.22 |
| Filtrate and leave the filtrated solution at 61 °C                                                             |      |
| Add 0.06 g of alum and leave 5 minutes stirring                                                                | 4.59 |
| Add 0.7 g of cream of tartar and leave 15 minutes stirring                                                     | 3.64 |
| Add 0.17 g of calcium carbonate and stir                                                                       | 4.59 |
| Centrifugate                                                                                                   |      |
| Dissolve the precipitate with 80 mL of $\text{H}_2\text{O}$                                                    | 5.00 |
| <i>To prepare the "body":</i>                                                                                  |      |
| Sift 0.9 g of plaster of Paris into 100 mL of $\text{H}_2\text{O}$ while stirring and leave two hours stirring | 7.44 |
| Centrifugate                                                                                                   |      |
| Add the "lake precipitate liquor" to the body while stirring                                                   | 5.70 |
| Centrifugate                                                                                                   |      |

**Table 9 (cont.).** Summary of the steps and pH values of the reconstructions of W&N's crimson lake and scarlet lake products (transcription of the original recipes in Appendix 4, pp.137-140).

|                                                                                                                               |      |
|-------------------------------------------------------------------------------------------------------------------------------|------|
| <b>Crimson Lake</b>                                                                                                           |      |
| <i>To prepare the "lake precipitate liquor":</i>                                                                              |      |
| Boil 250 mL of H <sub>2</sub> O                                                                                               | 5.80 |
| Turn off steam                                                                                                                |      |
| Add 3.0 g of ground cochineal                                                                                                 | 5.13 |
| Add 0.06 g of potassium carbonate                                                                                             | 6.00 |
| Add 0.1 g of alum                                                                                                             | 4.97 |
| Filtrate and leave the filtrated solution at 61 °C                                                                            |      |
| Add 0.06 g of alum and leave 5 minutes stirring                                                                               | 4.38 |
| Add 0.7 g of cream of tartar and leave 15 minutes stirring                                                                    | 3.47 |
| Add 0.17 g of calcium carbonate and stir                                                                                      | 4.44 |
| Centrifugate                                                                                                                  |      |
| Dissolve the precipitate with 20 mL of H <sub>2</sub> O                                                                       | 5.00 |
| <i>To prepare the "body":</i>                                                                                                 |      |
| Dissolve 0.3 g of ammonium carbonate into 20 mL of boiling H <sub>2</sub> O while stirring                                    | 7.88 |
| Dissolve 0.9 g of alum into 30 mL of boiling H <sub>2</sub> O while stirring                                                  | 3.26 |
| Add the alum into the ammonium carbonate as quickly as possible while stirring and leave 15 minutes stirring and centrifugate | 5.02 |
| Add the "lake precipitate liquor" to the body while stirring                                                                  | 5.13 |
| Centrifugate                                                                                                                  |      |
| <b>Scarlet Lake</b>                                                                                                           |      |
| <i>To prepare the "lake precipitate liquor":</i>                                                                              |      |
| Boil 250 mL of H <sub>2</sub> O                                                                                               | 5.30 |
| Turn off steam                                                                                                                |      |
| Add 3.0 g of ground cochineal                                                                                                 | 5.02 |
| Add 0.06 g of potassium carbonate                                                                                             | 6.10 |
| Add 0.1 g of alum                                                                                                             | 5.24 |
| Filtrate and leave at 61 °C                                                                                                   |      |
| Add 0.06 g of alum and leave 5 minutes stirring                                                                               | 4.58 |
| Add 0.7 g of cream of tartar and leave 15 minutes stirring                                                                    | 3.40 |
| Add 0.17 g of calcium carbonate and stir                                                                                      | 4.61 |
| Centrifugate                                                                                                                  |      |
| Dissolve the precipitate with 80 mL of H <sub>2</sub> O                                                                       | 4.52 |
| <i>To prepare the "body":</i>                                                                                                 |      |
| Dissolve 0.3 g of ammonium carbonate into 20 mL of boiling H <sub>2</sub> O while stirring                                    | 7.88 |
| Dissolve 0.9 g of alum into 30 mL of boiling H <sub>2</sub> O while stirring                                                  | 3.26 |
| Add the alum into the ammonium carbonate as quickly as possible while stirring and leave 15 minutes stirring                  | 4.20 |
| Add 0.4 g of vermilion and centrifugate                                                                                       | 4.10 |
| Add the "lake precipitate liquor" to the body while stirring                                                                  | 4.06 |
| Centrifugate                                                                                                                  |      |

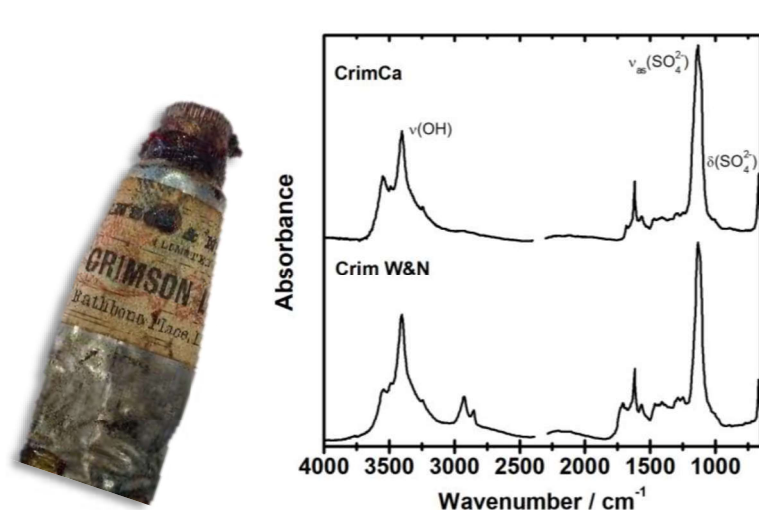


**Figure 22.** (Left) Historical tube of W&N crimson oil paint (Crim W&N). (Right) Infrared spectra of crimson pigment produced from W&N's main manufacturing processes (CrimCa) and historical W&N crimson oil paint (Crim W&N).

For the scarlet lake, the process was the same as for CrimAl with the further addition of vermilion (HgS) to the aluminate (pH 4). In this case, a final pigment with an orange reddish hue was obtained at pH 4-5 (Scarlet). Analysis of these reconstructions with infrared spectroscopy distinguishes between the crimson and scarlet lakes which show the aluminate compound, **Figure 21**, and the rough crimson lake made with the plaster of Paris, which shows the infrared fingerprint of gypsum, **Figure 22**. This distinction is expected due to the different infrared fingerprints associated with the different inorganic compounds. The aluminate shows its characteristic bands at 1647 cm<sup>-1</sup>, associated with OH deformation vibrations due to its amorphous nature, and 1110 cm<sup>-1</sup> attributed to the sulphate anions which can be incorporated into the substrate as it precipitates (Favaro et al. 2002; Kirby, Spring, and Higgitt 2005), while gypsum shows its infrared fingerprint with bands at 3400 cm<sup>-1</sup> ( $\nu(\text{HO})$ ), 1132 cm<sup>-1</sup> ( $\nu_{\text{as}}(\text{SO}_4^{2-})$ ) and 670 cm<sup>-1</sup> ( $\delta_{\text{as}}(\text{SO}_4^{2-})$ ) (Derrick, Stulik, and Landry 1999, p.117), see Subchapter 3.2.4, p.54. In both cases, the infrared spectra are clearly different from that obtained for the carmine pigments.

### 3.2.3. Purple Lake

The purple lake was obtained from a mixture of the extraction solutions with citric acid and potassium carbonate, with the further addition of cream of tartar, potassium carbonate, alum and zinc sulphate, following a record for a Best Deep Purple Lake,<sup>32</sup> **Table 10**. A purple pigment was obtained at a pH of 6-6.5 (Purple), which infrared spectrum shows a strong absorption band at 1600

<sup>32</sup> Several records for purple were reconstructed, most of which resulted in pigments which looked either too dark or too pinkish. The reconstruction of the Best Deep Purple Lake resulted in a bright purple colour, therefore it was chosen to integrate the set of representative reconstructions of cochineal lake pigments (see Subchapter 3.2.4, p.48).

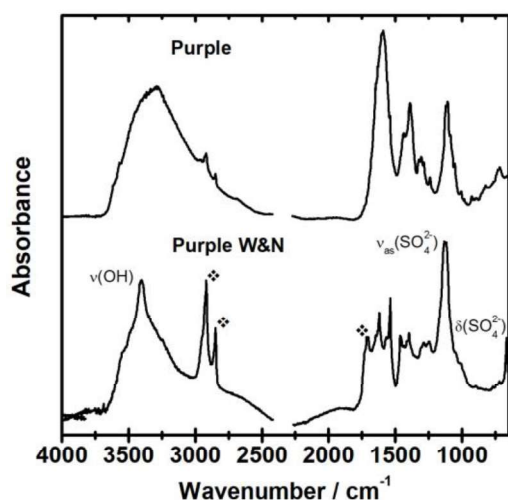


**Figure 23.** Infrared spectra of purple pigment produced from W&N's main manufacturing processes (Purple) and historical W&N purple oil paint (Purple W&N). Bands attributed to the oil binder are indicated with ❖.

cm<sup>-1</sup> and a well-structured fingerprint from 1490 cm<sup>-1</sup> to 1020 cm<sup>-1</sup> with two sharp bands at 1390 cm<sup>-1</sup> and 1113 cm<sup>-1</sup>, **Figure 23**. Although the assignment of these bands requires further investigation, elemental analysis revealed the presence of zinc, aluminium and calcium (see Subchapter 3.2.4, p.49), suggesting a complex with these three elements. This pigment, however, was not a match to the only purple historical sample available, an historical W&N tube of Purple Lake oil paint (Purple W&N), which infrared spectrum revealed the presence of gypsum, **Figure 23**.

**Table 10.** Summary of the steps and pH values of the reconstructions of W&N's purple lake products (transcription of the original recipe in Appendix 4, p.141).

| Steps                                                                 | pH   |
|-----------------------------------------------------------------------|------|
| <b>Purple Lake</b>                                                    |      |
| <i>To prepare "solution A":</i>                                       |      |
| Boil 350 mL of H <sub>2</sub> O                                       | 4.50 |
| Add 0.31 g of citric acid                                             | 1.30 |
| Add 5.0 g of ground cochineal                                         | 2.60 |
| Filtrate                                                              |      |
| Boil the cochineal in 350 mL H <sub>2</sub> O                         |      |
| Add 0.19 g of potassium carbonate                                     | 10.5 |
| Add 0.1 g of alum                                                     | 5.50 |
| Add 3.0 g of zinc sulphate dissolved in 5 mL H <sub>2</sub> O         | 4.40 |
| <i>The prepare "solution B":</i>                                      |      |
| Boil 350 mL of H <sub>2</sub> O                                       | 4.50 |
| Add 0.625 g of potassium carbonate                                    | 10.9 |
| Add 5.0 g of ground cochineal                                         | 7.20 |
| Add 0.313 g of alum                                                   | 7.00 |
| Filtrate                                                              |      |
| Add 5.0 g of cream of tartar                                          | 3.00 |
| Add 3.33 g of potassium carbonate dissolved in 17 mL H <sub>2</sub> O | 6.60 |
| Add "solution B" to "solution A"                                      | 6.90 |
| Add 1.0 g of zinc sulphate                                            | 5.30 |
| Add 0.5 g of alum                                                     | 4.00 |
| Add 0.5 g of potassium carbonate                                      | 6.40 |
| Centrifugate                                                          |      |

### 3.2.4. Characterisation of cochineal reconstructions

A summary of the seven representative reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes to produce Carmine, Crimson Lake, Scarlet Lake and Purple Lake, their ingredients, final pH and colour is presented in **Table 11**. For comparison purposes and validation of the historically accurate reconstructions, the five historical samples detailed in **Table 12** were used.

Characterisation of thirteen references (the seven historically accurate reconstructed pigments and five historical samples of pigments or tubes of oil paint plus a reference of carminic acid precipitated with aluminium<sup>33</sup>) by the complementary analytical techniques SERS (Surface Enhanced Raman Spectroscopy),  $\mu$ Raman (microRaman Spectroscopy),  $\mu$ FTIR (microFourier Transform Infrared Spectroscopy),  $\mu$ EDXRF (microEnergy Dispersive X-ray Fluorescence Spectrometry) and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry)<sup>34</sup> resulted in the identification of five main molecular complexes (herein designated as chromophores, which term was adapted from the definition presented in page 1), **Table 13**. Each chromophore presents a characteristic elemental and molecular fingerprint, which will be further discussed below. Additionally, W&N's manufacturing processes for crimson, scarlet and purple cochineal products can be further characterised by the presence of an amorphous substrate (aluminate), an extender (gypsum), or the inorganic pigment vermilion (HgS), identified through  $\mu$ EDXRF,  $\mu$ Raman and  $\mu$ FTIR.

**Table 11.** Description of the reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes to produce carmines, crimson, scarlet and purple lakes: ingredients, final pH and colour\*.

| W&N's products | Manufacturing process              | Ingredients                                                            | Final pH | Colour                                                                                | L* | a* | b* |
|----------------|------------------------------------|------------------------------------------------------------------------|----------|---------------------------------------------------------------------------------------|----|----|----|
| Carmine        | Finest Orient Carmine (FOC)        | Citric acid, milk, sodium borate, alum                                 | 5 - 5.5  |  | 31 | 45 | 19 |
|                | Half Orient Carmine (HOC)          | Citric acid, sodium borate, alum                                       | 4.5 - 5  |  | 34 | 35 | 1  |
|                | Fine Printing Carmine (FPC)        | Potassium carbonate, alum, cream of tartar, calcium carbonate          | 4 - 4.5  |  | 35 | 46 | 19 |
| Crimson        | Crimson with aluminate (CrimAl)    | FPC dispersion, aluminate                                              | 5 - 5.5  |  | 35 | 47 | 5  |
|                | Crimson with gypsum (CrimCa)       | FPC dispersion, gypsum                                                 | 5.5 - 6  |  | 34 | 33 | 3  |
| Scarlet        | Scarlet with aluminate (Scarlet)   | FPC dispersion, aluminate, vermilion                                   | 4 - 5.5  |  | 44 | 41 | 14 |
| Purple         | Purple with zinc sulphate (Purple) | Citric acid, potassium carbonate, cream of tartar, alum, zinc sulphate | 6 - 6.5  |  | 39 | 15 | -8 |

\* L\* a\* b\* colour coordinates measured on gum-arabic paints on glass slides with a portable spectrophotometer using the CIE illuminant D65 and 10° colorimetric standard observer.

<sup>33</sup> See Appendix 3, p.131.

<sup>34</sup> Details regarding the apparatus and experimental conditions used are presented in Appendix 3, p.128.

**Table 12.** Description of the historical samples of pigments and tubes of oil paint.<sup>35</sup>

| Type of sample | Name                                | Provenance                                                |
|----------------|-------------------------------------|-----------------------------------------------------------|
| Powder         | Finest Orient Carmine W&N (FOC W&N) | Winsor & Newton Archive                                   |
|                | Fine Printing Carmine W&N (FPC W&N) | Winsor & Newton Archive                                   |
| Oil paint      | Carmin Lefranc (Carmin LF)          | Amadeo de Souza-Cardoso (@DCR FCT/NOVA <sup>#</sup> )     |
|                | Crimson W&N (Crim W&N)              | Private collection (@DCR FCT/NOVA <sup>#</sup> )          |
|                | Purple Lake W&N (Purple W&N)        | Columbano Bordalo Pinheiro (MNAC collection) <sup>§</sup> |

<sup>#</sup> DCR FCT NOVA stands for Department of Conservation and Restoration of the NOVA School of Science and Technology.

<sup>§</sup> Columbano Bordalo Pinheiro (1857-1929) was a Portuguese painter, whose oil paints were donated to the Museu Nacional de Arte Contemporânea do Chiado - MNAC (National Museum of Contemporary Art - Museum of Chiado).

**Table 13.** Names and elemental analysis of the reference of carminic acid with aluminium, reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes and historical samples.

| Chromophore | Name                                            | Type of reference         | μEDXRF <sup>a</sup> /ICP-AES             |
|-------------|-------------------------------------------------|---------------------------|------------------------------------------|
| Lake CA-Al  | Carminic acid + Al <sup>3+</sup> (CA-Al)        | Pigment                   | Al                                       |
| Lake HOC    | Half Orient Carmine (HOC)                       | Pigment reconstruction    | Al, B                                    |
| Lake FOC    | Finest Orient Carmine (FOC)                     | Pigment reconstruction    | Ca, Al, B                                |
|             | Finest Orient Carmine W&N (FOC W&N)             | Historical pigment        | Ca, Al, B                                |
|             | Carmin Lefranc (Carmin LF)                      | Historical oil paint tube | Ca, Al, B                                |
| Lake FPC    | Fine Printing Carmine (FPC)                     | Pigment reconstruction    | Ca, Al                                   |
|             | Fine Printing Carmine W&N (FPC W&N)             | Historical pigment        | Ca, Al                                   |
|             | Crimson with aluminate (CrimAl) <sup>b</sup>    | Pigment reconstruction    | Ca, Al                                   |
|             | Crimson with gypsum (CrimCa)                    | Pigment reconstruction    | Ca, Al, S <sup>c</sup>                   |
|             | Crimson W&N (Crim W&N)                          | Historical oil paint tube | Ca, Al, S <sup>c</sup>                   |
|             | Scarlet with aluminate (Scarlet) <sup>b</sup>   | Pigment reconstruction    | Ca, Al, S <sup>d</sup> , Hg <sup>d</sup> |
| Lake Purple | Purple with zinc sulphate (Purple) <sup>b</sup> | Pigment reconstruction    | Ca, Zn, Al                               |
|             | Purple Lake W&N (Purple W&N)                    | Historical oil paint tube | Ca, Zn, Al                               |

<sup>a</sup> Only the main elements associated with the pigment's matrix are presented. Other elements such as K, Fe, Cl and P associated to contributions of the dyestuff raw materials (Kirby, Spring, and Higgitt 2005) and Sn, Mn and Ba (associated to the historical oil paint tubes) were detected in small amounts. See **Table 29**, Appendix 5, p.142.

<sup>b</sup> Analysed by μEDXRF only. Aluminium was assumed to be present due to the addition of alum and subsequent precipitation of pigment during the manufacturing processes.

<sup>c</sup> The element sulphur (S) is associated to the presence of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

<sup>d</sup> The elements sulphur (S) and mercury (Hg) are associated to the presence of vermilion (HgS).

<sup>35</sup> The historical samples of pigments and tubes of oil paint used were previously characterised with HPLC-DAD and the presence of carminic acid was confirmed.

ICP-AES analysis were carried out to identify the elements aluminium (Al), calcium (Ca), boron (B) and zinc (Zn) in the lake pigment reconstructions' matrix, adding up to the information gathered with  $\mu$ EDXRF. The main elements detected in the historical samples of pigments and tubes of oil paint, **Table 13**, show a good correspondence with those of the reconstructions. The complete set of results obtained with the two elemental analytical techniques, as well as representative  $\mu$ EDXRF spectra, are presented in Appendix 5, pp.142-144. Discussion of these results was made from a qualitative point of view since quantification of elements was not straightforward when comparing between reconstructions of pigments and historical paint samples.

As shown in **Table 13**, the five chromophores identified (lakes CA-Al, HOC, FOC, FPC and Purple) are characterised by specific elements. The simplest chromophore, lake CA-Al, is associated with the carminic acid-aluminium reference, in which only Al was detected. Analysis of the cochineal lake pigments reconstructed following W&N's manufacturing processes also revealed the presence of Al in the pigments' structure due to the addition of alum. Ca was detected in significant amounts in all reconstructions except for the HOC. The presence of this element is associated with the addition of milk in the FOC process and, in the remaining processes, with what the author considers to have been an impure cream of tartar, which likely contained calcium tartrate in its composition, as previously mentioned (see Subchapter 3.2.1, pp.39-43). The simultaneous presence of Al and Ca, forming a complex of carminic acid with these elements, turned out to be essential to obtain a carmine colour. On the contrary, the absence of Ca produced pigments with a purple hue. Boron (B), from sodium borate, was also detected in the Finest and Half Orient Carmine processes acting as a marker for the acid extraction method and suggesting its presence in the pigments' structure. These three elements identify lake HOC (Al, B), lake FOC (Ca, Al, B) and lake FPC (Ca, Al). Within lake FPC, mercury (Hg) is a marker for the scarlet manufacturing processes and the presence of sulphur (S) in significant amounts and disassociated with Hg may be a marker for the crimson lakes with gypsum. A fifth chromophore, lake Purple, is associated to the purple lake which is characterised by the presence of Zn.

For comparison with the SERS results obtained for the reconstructions of W&N cochineal lake pigments, the spectrum of carminic acid was acquired following the same direct nonextractive nonhydrolysis SERS approach, **Figure 24**, which correlated well with those presented in the literature (Whitney, Van Duyne, and Casadio 2006; Chen et al. 2006; Leona, Stenger, and Ferloni 2006; Brosseau et al. 2009; Pozzi et al. 2014). The assignments of SERS spectra of carminic acid in solution has been derived by Cañamares et al. 2006 from calculations carried out using the density

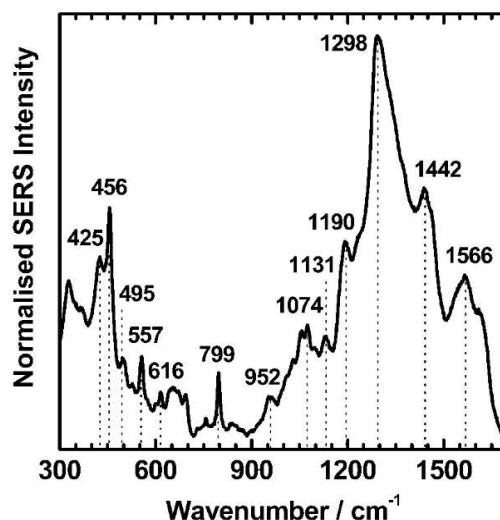


**Figure 24.** SERS spectrum of carminic acid.

functional theory (DFT) method, **Table 14**. These authors have shown that the SERS spectrum of carminic acid can vary depending on changes in its chemical environment. Accordingly, variations are expected when carminic acid is complexed with different metal ions.

**Table 14.** Selected SERS wavenumbers and assignments of carminic acid (based on Cañamares et al. 2006).

| Wavenumbers / $\text{cm}^{-1}$ | Assignments <sup>#</sup>                                                                                         |
|--------------------------------|------------------------------------------------------------------------------------------------------------------|
| 1566                           | $\nu(\text{CC})$ , $\delta(\text{COH})$ , $\delta(\text{CH})$                                                    |
| 1442                           | $\nu(\text{CC})$ , $\delta(\text{CH}_3)$ , $\delta_{\text{Glu}}(\text{CH})$                                      |
| 1298                           | $\delta(\text{C}_5\text{OH})$ , $\delta(\text{C}_8\text{OH})$ , $\delta(\text{C}_3\text{OH})$ , $\nu(\text{CC})$ |
| 1131                           | $\nu(\text{CC})$ , $\delta(\text{COH})$ , $\delta(\text{CH})$                                                    |
| 1074                           | $\nu_{\text{Glu}}(\text{C-O})$ , $\delta_{\text{Glu}}(\text{COH})$                                               |
| 952                            | $\delta(\text{CCC})$ , $\rho(\text{CH}_3)$                                                                       |

<sup>#</sup>  $\nu$ , stretching;  $\delta$ , in-plane bending;  $\rho$ , rocking; Glu, glucose moiety

The nonextractive nonhydrolysis SERS approach carried out directly in the reconstructions of W&N cochineal lake pigments allowed to obtain reproducible spectra with a good SERS signal, **Figure 25**. These spectra are indeed different in comparison with that of the carminic acid itself, showing the disappearance of bands and appearance of new vibrations, which reveals a fingerprint of carminic acid in its complexed form. All spectra show similar features, which have also been presented by Bruni, Guglielmi, and Pozzi 2011 and Zaffino et al. 2014 as characteristic of a cochineal and a cochineal carmine spectrum, respectively. Sharp bands at the lower energies 657, 731 and 952  $\text{cm}^{-1}$ , which are inexistent or very weak in the spectrum of carminic acid, are present in all spectra of the lake pigment reconstructions with different relative intensities. In the literature, these bands have been assigned to the rocking mode of the methyl group in carminic acid and to bending

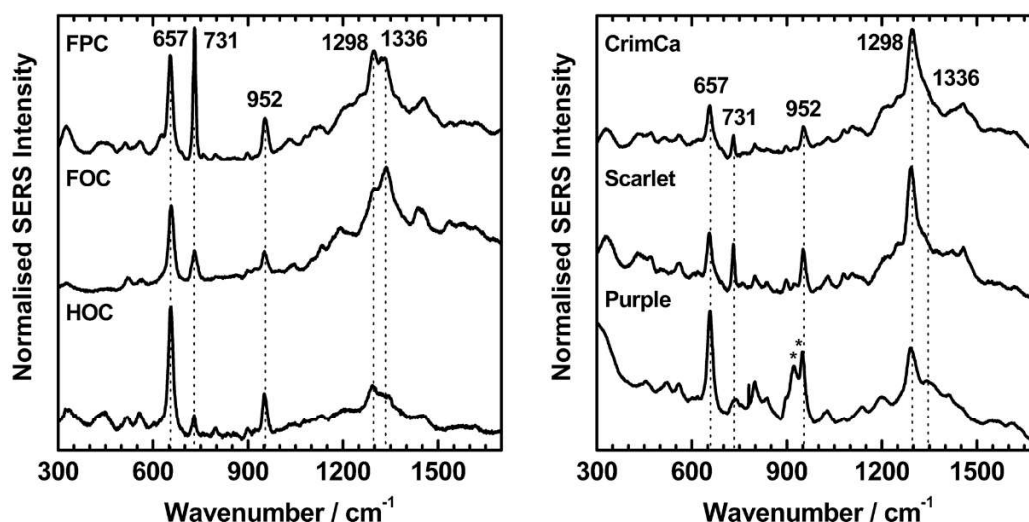


**Figure 25.** SERS spectra of the reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes: FPC, FOC, HOC, CrimCa, Scarlet and Purple. Bands attributed to the silver colloid are indicated with an asterisk.

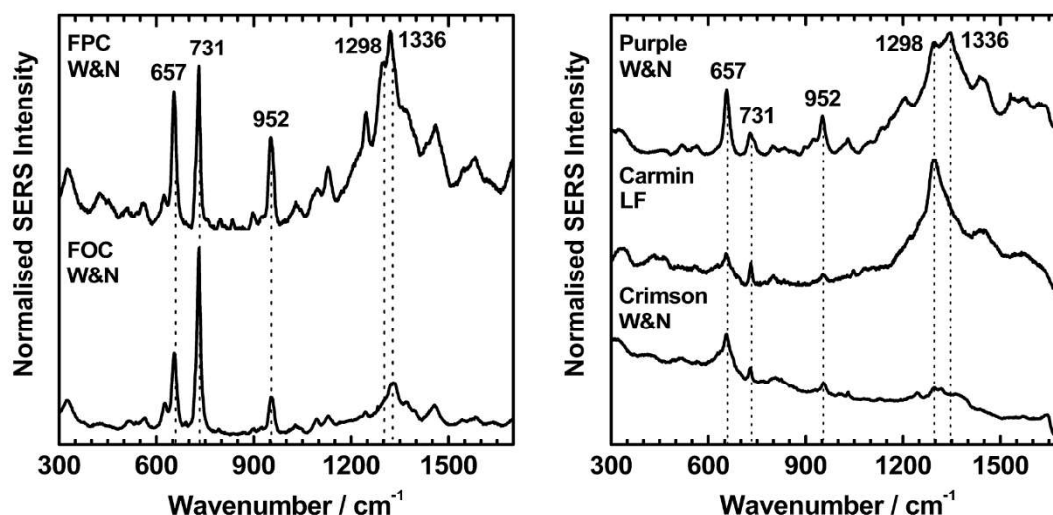


**Figure 26.** SERS spectra of the historical pigments (FPC W&N and FOC W&N), and paints from tubes of oil paint (Purple W&N, Carmin LF and Crim W&N).

modes of CH, COH and CCC (Cañamares et al. 2006; Bruni, Guglielmi, and Pozzi 2011). Also present with different intensities in the lake pigment reconstructions' spectra are the bands at ca. 1298 and 1336  $\text{cm}^{-1}$ . The 1298  $\text{cm}^{-1}$  band is the most intense in the spectrum of carminic acid, **Figure 24**, and has been assigned to the in-plane bending vibrations of  $\text{C}_5\text{OH}$ ,  $\text{C}_8\text{OH}$  and  $\text{C}_3\text{OH}$ , coupled to ring-stretching vibrations [ $\nu(\text{CC})$ ] (Cañamares et al. 2006). The second band, at 1336  $\text{cm}^{-1}$ , has been assigned to the COH bending mode of the carboxylic group in carminic acid (Cañamares et al. 2006; Bruni, Guglielmi, and Pozzi 2011). The relative intensities of these two bands at 1298 and 1336  $\text{cm}^{-1}$  in the reconstructions' spectra was found to vary within the same samples. The observed variations can be attributed to different interaction modes of the analyte on the surface of the nanoparticles (Jurasekova et al. 2010; Retko, Ropret, and Korošec 2014). This interaction has been suggested to occur between free hydroxyl or hydroxyl-keto groups of carminic acid and the silver colloid, possibly with formation of chelate rings with the silver atoms (Idone et al. 2014). The lower relative intensity of these bands when compared with the spectrum of carminic acid may be an indication that the hydroxyl groups in the lake pigment reconstructions are partially occupied by interactions with complexing ions ( $\text{Al}^{3+}$ ).

The nonextractive nonhydrolysis SERS approach carried out directly in the historical samples of pigments and tubes of oil paint allowed to obtain reproducible spectra with a good SERS signal too, **Figure 26**. In particular, the good signal obtained with the historical oil paint tubes, allowing the detection of the metal complex of carminic acid, was a positive outcome since the interference of the binder was an expected obstacle to the direct SERS analysis of these samples. An exception was found for the Crim W&N oil paint tube, which presented a lower SERS signal. For this sample, a good Raman spectrum was obtained, **Figure 27**, in which it was possible to identify the extender gypsum, characteristic of one of W&N's crimson manufacturing process. In all SERS spectra of the historical samples, the same bands at ca. 657, 731, 952, 1298 and 1336  $\text{cm}^{-1}$ , again with different relative intensities, were observed.

The results obtained with the direct SERS approach did not allow to distinguish between the

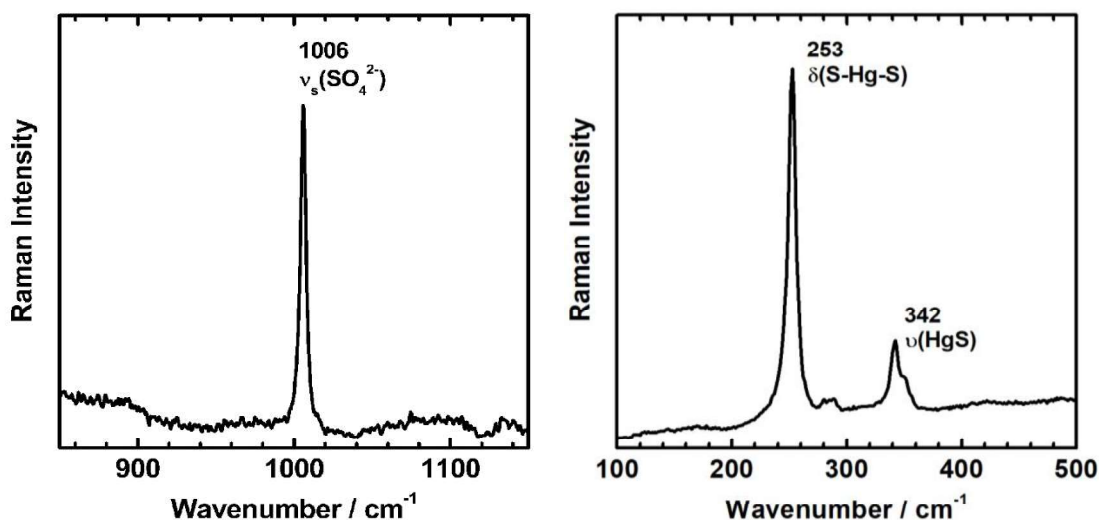


**Figure 27.** Raman spectrum of (left) the historical paint from tube of oil paint Crim W&N and (right) the reconstruction of cochineal lake pigment prepared from W&N's scarlet manufacturing process (collected with an external laser operating at 785 nm with an exposure time of 20 seconds for 20 scans; spectra are shown after baseline correction).

different cochineal chromophores obtained with W&N's manufacturing processes, **Table 13**. The bands observed in all SERS spectra of the lake pigment reconstructions and historical samples may be proposed as indicators of metal complexes of carminic acid without any need for a hydrolysis step which would break the integrity of the sample. This can be extremely relevant when the sample contains high amounts of inorganic substrate (generally, an amorphous aluminate), extenders such as gypsum, or binders, which can mask the fingerprint of the chromophore. On the other hand, the application of a nonextractive nonhydrolysis approach allows the afterwards removal of the silver colloid from the sample which can be kept for further analysis that may help to identify the chromophore (Pozzi et al. 2012). However, before the proposed bands can be used as unambiguous markers for complexes of carminic acid, further studies must be carried out using the same SERS approach on references of other anthraquinone-based complexes. It is particularly important to study complexes of kermesic acid, the aglycone of carminic acid, due to the similarity between the molecular structures of the two anthraquinones which can lead to similar interactions with the nanoparticles.

As previously shown, the infrared results obtained for the historical samples of pigments and tubes of oil paint allowed for the validation of the reconstructions of W&N cochineal lake pigments, **Figures 18-22**, pp.40-46. A match was found between the historical pigment samples FOC W&N and FPC W&N and the reconstructions FOC and FPC, respectively. The samples of historical oil paint tubes revealed, as well, a spectral fingerprint similar to the corresponding pigments' reconstructions, in addition to the presence of the oil binder. Particularly, the sample of Carmin LF was a match to the FOC sample. The Crim W&N, which compares with the reconstruction CrimCa, revealed the further presence of gypsum, which characteristic infrared bands have been described in Subchapter 3.2.2, p.46.

Similarly to the SERS results, all infrared spectra of the reconstructions of W&N cochineal lake

pigments are different in comparison with that of the carminic acid itself. However, through this analytical technique it was possible to identify the different chromophores presented in **Table 13**, as discussed below. As described in Subchapter 3.2.2, p.46, the identification of the additives characteristic of the W&N manufacturing processes for crimson and scarlet cochineal products, **Table 13**, was also very straightforward. The infrared spectra of the crimson and scarlet products with aluminate, **Figure 21**, Subchapter 3.2.2, p.44, show its characteristic bands at  $1647\text{ cm}^{-1}$ , associated with OH deformation vibrations due to its amorphous nature, and  $1110\text{ cm}^{-1}$  attributed to the sulphate anions which can be incorporated into the substrate as it precipitates (Favaro et al. 2002; Kirby, Spring, and Higgitt 2005). The crimson lake with gypsum shows its infrared fingerprint with bands at  $3400\text{ cm}^{-1}$  ( $\nu(\text{HO})$ ) and at  $1132$  and  $670\text{ cm}^{-1}$  for the stretching and bending of the sulphate ion, respectively (Derrick, Stulik, and Landry 1999, p.117). In these cases, it is also possible to detect bands of lower intensity in the  $1600\text{--}1200\text{ cm}^{-1}$  range, which correspond to the vibrations of the respective chromophore (lake FPC, **Figure 28**). The scarlet reconstruction was further analysed with  $\mu\text{Raman}$  to confirm the presence of vermilion which was detected through its characteristic bands at  $342\text{ cm}^{-1}$  ( $\nu(\text{HgS})$ ) and  $253$  and  $282\text{ cm}^{-1}$  ( $\delta(\text{S-Hg-S})$ ) (Otero 2018, p.254 and references cited therein), **Figure 27**.

The infrared spectra from  $2000$  to  $650\text{ cm}^{-1}$  of lakes CA-Al, HOC, FOC and FPC, and of carminic acid are presented in **Figure 28**. Assignments of carminic acid's vibrations have also been carried out by Cañamares et al. 2006. The main absorption bands of its infrared spectrum and the respective assignments are listed in **Table 15**. It is noteworthy that the greater contributions are due to vibrations related with the aromatic system of carminic acid. The differences found between its spectrum and the spectra of the reconstructions confirm that complexation with the different ions induces electronic delocalization in the aromatic system of carminic acid that leads to a different

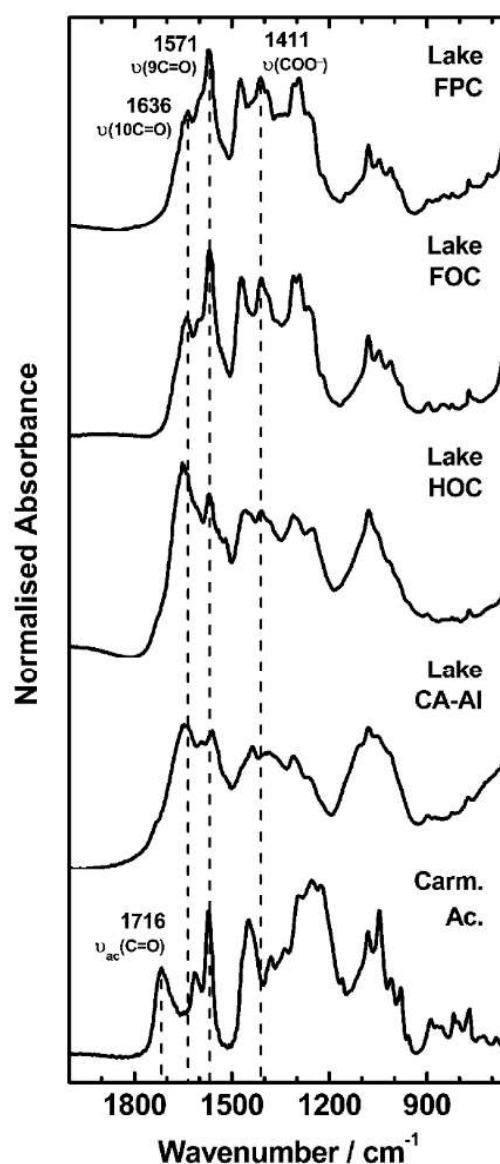


**Figure 28.** Infrared spectra from  $2000$  to  $650\text{ cm}^{-1}$  of carminic acid (Carm. Ac.), reference of carminic acid with aluminium (Lake CA-Al), and reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes (Lake HOC, Lake FOC and Lake FPC).

molecular structure. Particularly important for the discussion presented below regarding those differences are the bands at 1716  $\text{cm}^{-1}$  (attributed to the stretching of C=O in the carboxylic acid), 1614  $\text{cm}^{-1}$  (stretching of 9- and 10-C=O coupled with the stretching of CC bonds) and 1571  $\text{cm}^{-1}$  (stretching of CC together with bending vibrations of C<sub>5</sub>OH and CH) (Cañamares et al. 2006). Based on the asymmetry of the molecule and DFT calculations carried out for alizarin (Angelin, Teixeira, and Melo 2017), it is also possible that the band at 1614  $\text{cm}^{-1}$  is mostly influenced by the stretching vibration of the 10-C=O, while the 1571  $\text{cm}^{-1}$  band has contributions from the 9-C=O.

The infrared spectra of lake CA-Al, lake HOC and lake FOC, **Figure 28**, reveal distinct fingerprints which are indicative of different molecular structures involving characteristic chemical elements (**Table 13**). An exception is found for boron (B), which presence in the molecular structure is not clear through observation of the infrared spectra of lake FOC and lake FPC, which are very similar.

**Table 15.** Selected infrared wavenumbers and assignments of carminic acid (based on Cañamares et al. 2006) and lakes CA-Al, HOC, FOC and FPC.

| Wavenumbers / $\text{cm}^{-1}$ * |            |            |            |            | Assignments <sup>#</sup>                                                                        |
|----------------------------------|------------|------------|------------|------------|-------------------------------------------------------------------------------------------------|
| Carminic acid                    | Lake CA-Al | Lake HOC   | Lake FOC   | Lake FPC   |                                                                                                 |
| ca. 3348br                       | ca. 3405br | ca. 3348br | ca. 3383br | ca. 3406br | v(OH)                                                                                           |
| 2943w                            | 2919m      | 2923m      | 2934w      | 2935w      | v(CH <sub>3</sub> ), v <sub>Glu</sub> (CH)                                                      |
| 1716m                            |            |            |            |            | v <sub>acid</sub> (C=O)                                                                         |
|                                  | 1647m      | 1653s      | 1637m      | 1635m      |                                                                                                 |
| 1614m                            |            |            |            |            | v(C=O), v(CC)                                                                                   |
| 1571s                            | 1560m      | 1570m      | 1569s      | 1573s      | v(CC), $\delta$ (C <sub>5</sub> OH), $\delta$ (CH)                                              |
|                                  | 1472sh     | 1458m      | 1471m      | 1474m      |                                                                                                 |
| 1448s                            |            |            |            |            | v(CC), $\delta$ (CH <sub>3</sub> ), $\delta$ <sub>Glu</sub> (CH)                                |
|                                  |            | 1409m      | 1411m      | 1412m      | v(COO <sup>-</sup> )                                                                            |
| 1380m                            | 1386w      |            |            |            | $\delta$ <sub>Glu</sub> (CH), $\delta$ <sub>Glu</sub> (COH), $\delta$ (COH)                     |
| 1338w                            |            |            |            |            | $\delta$ <sub>acid</sub> (COH), $\delta$ (C <sub>5</sub> OH), $\delta$ <sub>Glu</sub> (CH)      |
| 1295w                            |            |            | 1292m      | 1293m      | $\delta$ (C <sub>5</sub> OH), $\delta$ (C <sub>8</sub> OH), $\delta$ (C <sub>3</sub> OH), v(CC) |
| 1254s                            | 1261sh     | 1250w      | 1265w      | 1265w      | v(CC), $\delta$ <sub>acid</sub> (COH), $\delta$ (COH), $\delta$ <sub>Glu</sub> (CH)             |
| 1227w                            |            |            | 1223sh     | 1220sh     | $\delta$ (C <sub>5</sub> OH), $\delta$ (C <sub>4</sub> H), $\delta$ <sub>Glu</sub> (CH)         |
| 1081m                            | 1080m      | 1080s      | 1080m      | 1080m      | v <sub>Glu</sub> (C-O), $\delta$ <sub>Glu</sub> (COH)                                           |
| 1046s                            | 1050sh     | 1050sh     | 1048m      | 1047m      | v <sub>Glu</sub> (C-C), $\delta$ <sub>Glu</sub> (COH)                                           |
| 1012m                            | 1013sh     | 1013sh     | 1012m      | 1012m      | v(CC), $\delta$ (CCC)                                                                           |
| 980m                             |            |            | 983sh      | 980sh      | $\delta$ (CCC), $\rho$ (CH <sub>3</sub> )                                                       |

\* br, broad; s, strong; m, medium; w, weak; sh, shoulder

<sup>#</sup> v, stretching;  $\delta$ , in-plane bending;  $\rho$ , rocking; Glu, glucose moiety

Comparing between the infrared spectra of the four chromophores under study, a main finding

regarding their molecular structure has been achieved: lakes CA-Al and HOC, without Ca, show broader and less structured absorption bands, while lakes FOC and FPC, both with Al and Ca, present well-structured fingerprints. The broadening and loss of structure is clearly visible, for example, in the bands corresponding to the glucose unit of carminic acid (1081 and 1046  $\text{cm}^{-1}$ ). In comparison with the bands in carminic acid's spectrum described above, the disappearance of the band at 1716  $\text{cm}^{-1}$  and the appearance of a band at ca. 1411  $\text{cm}^{-1}$  that can be assigned to the symmetric stretching vibration of carboxylate ion ( $\text{COO}^-$ ), indicates that lake formation involves deprotonation of the carboxylic acid moiety, as expected. It can therefore be proposed that Ca, present in both lakes FOC and FPC, is bound to the carboxylate moiety of carminic acid. Moreover, the band at 1614  $\text{cm}^{-1}$  in carminic acid appears to have shifted to ca. 1636, which might be evidence that coordination with the  $\text{Al}^{3+}$  ion is taking place through the oxygen atoms of the 10-ketonyl and of the 5-hydroxyl group as is generally proposed in the literature (Favaro et al. 2002). This suggestion is supported by shifts in the bands at 1295 and 1227  $\text{cm}^{-1}$  (both with contributions of  $\delta(\text{C}_5\text{OH})$ ) in carminic acid. On the other hand, the less structured pattern of lakes CA-Al and HOC, with bands at ca. 1650 and 1560  $\text{cm}^{-1}$  (lake CA-Al) and 1650, 1570 and 1409  $\text{cm}^{-1}$  (lake HOC), suggests the presence of a mixture of isomers with different relative orientations of the carminic acid moieties around the complexing  $\text{Al}^{3+}$  ions (of which the structure presented in **Figure 10**, Subchapter 1.2.2, p.17, is one of the possible isomers). It is suggested that the binding of  $\text{Ca}^{2+}$  to the carboxylate moieties of carminic acid aligns the ligands for  $\text{Al}^{3+}$  binding hindering the formation of isomers. Consequently, when Ca is present in the pigments, well-structured infrared fingerprints are observed while its absence results in less constraints for the ligands, with concomitant formation of isomers

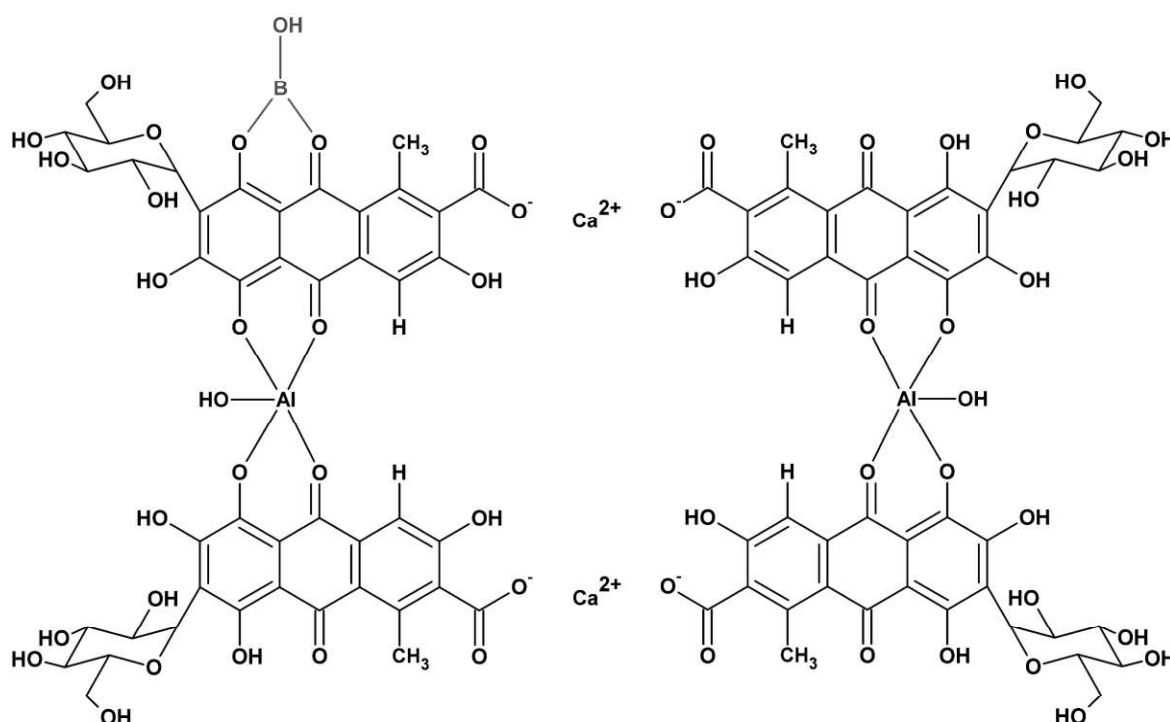


**Figure 29.** Possible structure for cochineal lake pigments prepared from W&N's manufacturing processes FPC (lake with Al and Ca) and FOC (lake with Al, Ca and B; the borate moiety is simulated in only one molecule of carminic acid).

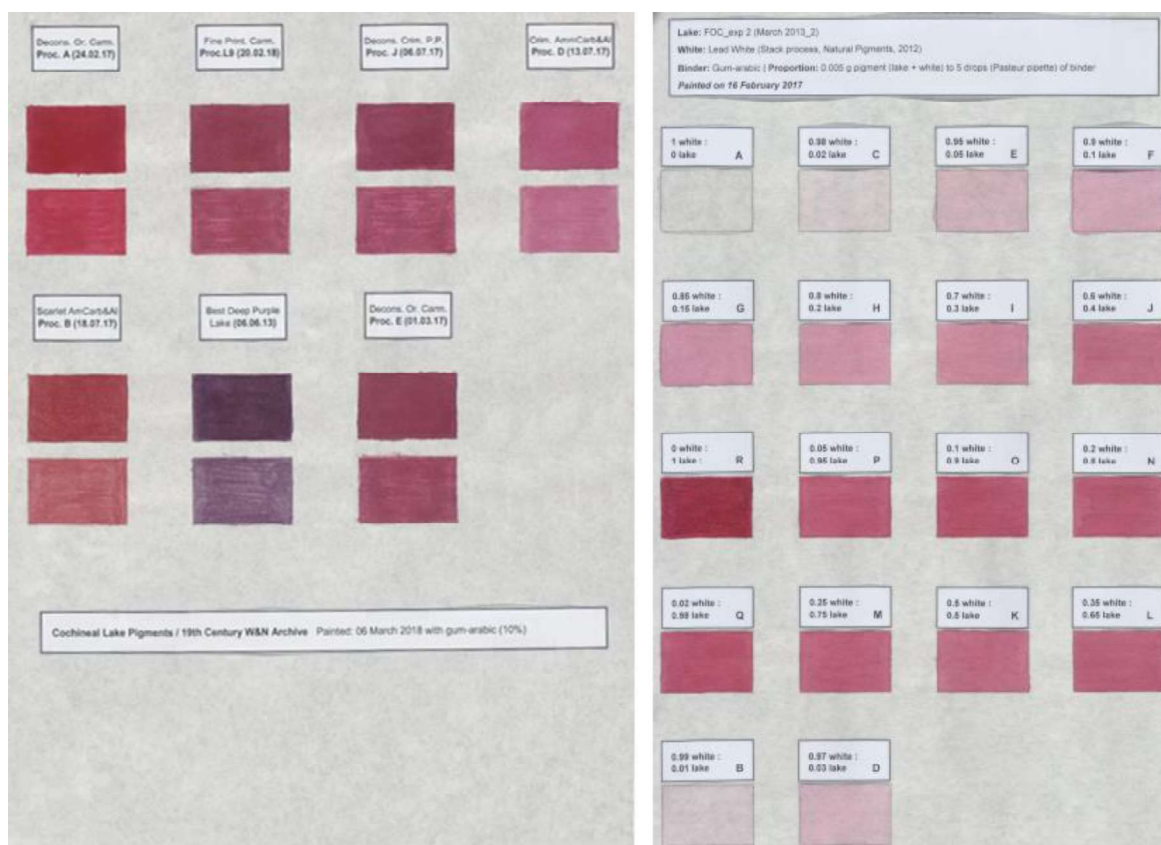


**Figure 30.** Gum-arabic paints on filter paper: (left) cochineal pigments reconstructed from W&N's main manufacturing processes (FOC, FPC, CrimCa, CrimAl, Scarlet, Purple and HOC) and (right) FOC mixed with lead white.

and less resolved spectra.

Finally, as noted above, the presence of B in the molecular structure of lake FOC does not seem to produce significant changes in the infrared spectrum. Nonetheless, B is known to form complexes with carminic acid (Floquet et al. 2016). A possible location for its coordination, in the form of borate ion, without affecting the structure of the complex formed between carminic acid, Al and Ca, is the 9-C=O and the hydroxyl group in position 8. In lake FPC this carbonyl group is possibly bonded with the 8-hydroxyl group through an hydrogen bond. The B-O bonds, which give strong infrared bands in the 1380-1310  $\text{cm}^{-1}$  range (Shurvell 2002), are possibly masked by the bands related with the aromatic system of the complex. Comparing between the infrared spectra of lakes CA-Al and HOC, the differences observed are less subtle possibly due to the existence of isomers with different geometries with and without B.

Based on these results, a preliminary suggestion of structure for the complexes with Al and Ca is presented in **Figure 29**. The borate ion is added in only one molecule of carminic acid to simulate its presence in the complex with Al, Ca and B (lake FOC). To corroborate the interpretations made and assist the definition of the corresponding molecular structures, prediction of spectra through DFT methods (Pagliai et al. 2018), as well as  $^{13}\text{C}$  and  $^{27}\text{Al}$  solid state nuclear magnetic resonance spectroscopy (NMR), should be carried out.

The reconstructed cochineal lake pigments were also painted with gum-arabic, a polysaccharide

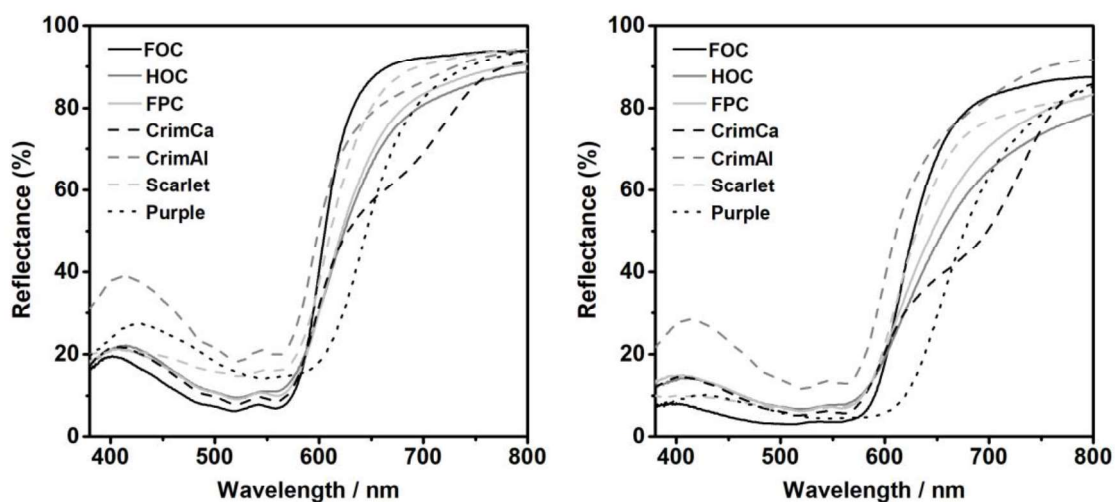


**Figure 31.** Reflectance spectra of cochineal pigments reconstructed from W&N's main manufacturing processes (left: less concentrated paints; right: more concentrated paints). Samples were mixed with gum-arabic and painted onto filter paper.

binder, and mixed with the pigments vermilion, cobalt blue and lead white, on filter paper, which paints are available for future researches, **Figure 30**. The paints were characterised with FORS and  $\mu$ spectrofluorimetry, which characteristic spectra are presented in **Figures 31** and **32**. Cochineal, being an anthraquinone molecule, has an absorption behaviour in the visible region which is related to the lowest energy  $\pi, \pi^*$  electronic transition, attributed to the conjugated double bonds and characterised by a significant charge-transfer contribution, and the  $n, \pi^*$  electronic transitions of the carbonyl groups (Miliani, Romani, and Favaro 1998; Bisulca et al. 2008; Kunkely and Vogler 2011). The FORS reflectance spectra of cochineal materials generally present two absorption sub-bands characteristic of the chromophore. The reflectance pattern of the spectra also provides information on the colour obtained, whether it is lighter (less concentrated) or darker (more concentrated). For the less concentrated paints obtained with the reconstructions of cochineal lake pigments, **Figure 31** and **Table 16**, with the exception of the Purple, the first absorbance sub-band varies from 519 nm to 521 nm and the second sub-band from 555 nm to 560 nm. The inflection point goes from 595 nm (crimsons) to 600-606 nm (carmines and Scarlet). The CrimCa is the only one presenting two inflection points, the second one at 720 nm. The Purple presents an absorbance at 547 nm and inflection point at 640 nm. In the more concentrated paints, **Figure 31**, the absorption sub-bands become harder to distinguish. The first absorbance sub-band varies from 516 nm to 522 nm and the second sub-band from 552 nm to 559 nm. The inflection point goes from 597 nm (crimsons) to 610-613 nm (carmines and Scarlet). The second inflection point of CrimCa appears at 730 nm. The Purple presents an absorbance at 544 nm and inflection point at 655 nm.

$\mu$ spectrofluorimetry complements the reflectance data and allows the discrimination between different environments of the chromophores, which can provide insight into the pigments' manufacturing processes, **Figure 32** and **Table 16**. In particular, the emission spectra discriminate between the carmines (FOC, HOC and FPC), which present broad spectra centred at 590 nm, and the crimsons (CrimCa and CrimAl), Scarlet and Purple, which spectra present maxima around 575

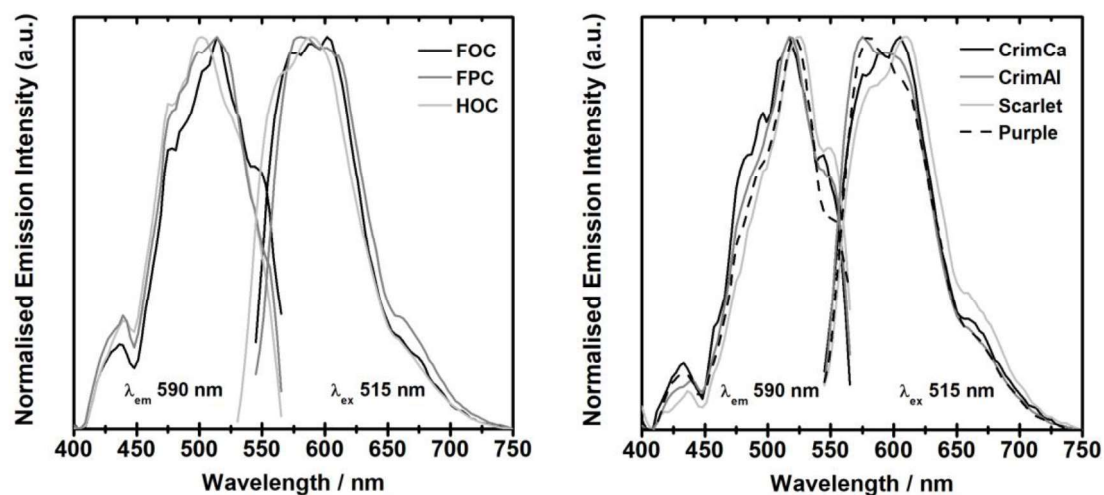


**Figure 32.** Excitation and emission spectra of cochineal pigments reconstructed from W&N's main manufacturing processes. Samples were mixed with gum-arabic and painted onto filter paper.

nm and 610 nm. The corresponding excitation spectra present maxima at 514 nm for FOC and FPC, at 502 nm for HOC, and around 520 nm for the crimsons, Scarlet and Purple.

**Table 16.** Absorption ( $\lambda_{abs1}$  and  $\lambda_{abs2}$ ), excitation ( $\lambda_{exc}$ ) and emission ( $\lambda_{em}$ ) maxima for cochineal pigments reconstructed from W&N's main manufacturing processes painted with gum-arabic on filter paper.

|         | $\lambda_{abs1}$ / nm | $\lambda_{abs2}$ / nm | $\lambda_{exc}$ / nm | $\lambda_{em}$ / nm |
|---------|-----------------------|-----------------------|----------------------|---------------------|
| FOC     | 519                   | 558                   | 514                  | 600                 |
| HOC     | 520                   | 555                   | 502                  | 590                 |
| FPC     | 520                   | 559                   | 514                  | 580                 |
| CrimCa  | 519                   | 559                   | 517                  | 605                 |
| CrimAl  | 521                   | 560                   | 517                  | 575                 |
| Scarlet | 520                   | 560                   | 525                  | 610                 |
| Purple  | 547                   |                       | 521                  | 580                 |



## Chapter 4

# Accelerated Light Ageing of Cochineal References

This chapter starts with the accelerated light ageing experience carried out in selected cochineal references, which results were followed by  $\mu$ FTIR,  $\mu$ spectrofluorimetry, FORS and colorimetry. It is followed by a section on microfading spectrometry, a relatively new method, which development and acceptance may benefit from comparisons between microfading tests and conventional accelerated light ageing techniques to support the correct interpretation of the data obtained. It includes a general introduction to the technique of microfading and a comparison between results obtained with both methods of artificial light ageing. This chapter concludes with an introduction to Vis-NIR reflectance hyperspectral imaging, which is followed by the application of this technique towards the interpretation of the results obtained with the accelerated light ageing experience.

Chapter 4 was executed in collaboration with Andrea Casini, Lorenzo Stefani and Costanza Cucci regarding the hyperspectral imaging section and Julio del Hoyo-Meléndez regarding the microfading technique.

Part of this chapter resulted in a web publication (COSCH e-Bulletin, 2015, 2, 1-6),<sup>36</sup> a peer-reviewed journal publication (Vitorino et al. 2015), an oral communication at the Sustainability in

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<sup>36</sup> Casini, A., Cucci, C., Picollo, M., Stefani, L., Vitorino, T. Creation of a Hyper-spectral Imaging Spectroscopy Reference Database of Red Lake Pigments. In: Bentkowska-Kafel, A. & Murphy, O. eds. *COSCH e-Bulletin*, 2015. No. 2, pp. 1-6.

Cultural Heritage Conference, Rome, 11-12 January 2016,<sup>37</sup> and two poster presentations at the Scientific Methods in Cultural Heritage Research Gordon Research Conference, Castelldefels, 22-27 July 2018,<sup>38</sup> and at the 37<sup>th</sup> International Conference for Dyes in History and Archaeology, Lisbon, 25-26 October 2018.<sup>39</sup>

#### 4.1. Accelerated light ageing with a solarbox

Following Loon, Noble, and Burnstock 2012 own words, ageing processes are inherent to the composition of paints, which stability can be affected by the different manufacturing processes and raw materials used. Not only that, pigment combinations, different binding media and their proportion to the pigment in the paint, the use of additives and/or extenders, layer build-up and thickness are all variables that determine the chemical environment of the materials and can influence their reactivity. Ageing processes can be triggered or accelerated by environmental conditions such as light, moisture, and heat. Colours may fade or completely disappear, and paint can become more transparent and yellower or appear darker. With natural organic red lake pigments, the type of degradation commonly associated is fading as a result of photochemical (light induced) degradation (Loon, Noble, and Burnstock 2012, pp.220,237 and references cited therein).

In this sense, to address the contribution of the pigment and the binder to the paint stability of cochineal products, an accelerated light ageing experience was carried out in a set of 15 paints prepared with selected cochineal references and two different binders, **Table 17**, painted in individual glass slides (1.5 x 2.5 cm). Twelve out of the 15 cochineal paints were made with reconstructions of Winsor & Newton 19th century Carmine (FOC and FPC), Crimson Lake (CrimAl and CrimCa), Scarlet Lake (Scarlet) and Purple Lake (Purple) pigments. Seven of these paints were prepared with gum-arabic (GA), while the other 6 paints were prepared with poly(vinyl acetate) (PVAc,  $[\text{CH}_2\text{CH}(\text{O}_2\text{CCH}_3)]_n$ ) which intended to simulate the role of oil since PVAc contains ester groups as the oil binder with the advantage of quickly air drying. The remaining 3 out of the 15 cochineal paints were prepared with historical samples of Carmine (FOC W&N and FPC W&N) and Purple (Purple W&N) cochineal lake pigments from Winsor & Newton and gum-arabic.

The paints were subjected to artificial irradiation for a period of time of 2000 hours in an accelerated light ageing apparatus (CO.FO.ME.GRA SOLARBOX 3000e, "Cofomegra Solarbox,"

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<sup>37</sup> Picollo, M., Vitorino, T., Casini, A., Cucci, C., Stefani, L. Hyperspectral imaging technique for the study of red lake pigments. Oral presentation at the *Sustainability in Cultural Heritage Conference 2016*, Rome, Italy, 11-12 January 2016.

<sup>38</sup> Vitorino, T., Otero, V., Carlyle, L., Parola, A. J., Melo, M. J., Picollo, M. Unique insights into the chemistry and photodegradation of 19th century artist's cochineal lake pigments. Poster presentation at the *Scientific Methods in Cultural Heritage Research Gordon Research Conference*, Castelldefels, Spain, 22-27 July 2018.

<sup>39</sup> Vitorino, T., Otero, V., Hoyo-Meléndez, J. M., Melo, M. J., Parola, A. J., Picollo, M. An investigation of the photostability of 19th century artist's cochineal lake pigments: artificial light aging vs microfading spectrometry. Poster presentation at the *37th annual international conference for Dyes in History and Archaeology*, Lisbon, Portugal, 25-26 October 2018.

n.d.) equipped with a high-intensity Xenon light source with an indoor UV filter ( $320 \leq \lambda_{irr} \leq 820$  nm), see **Figure 42**, Subchapter 4.3, p.77. The temperature and relative humidity inside the ageing apparatus were ca. 25 °C and ca. 40%, respectively. The  $L^* a^* b^*$  colour coordinates<sup>40</sup> of the paints exposed to irradiation were measured after different irradiation times (100 hours, 250 hours, 500 hours, 1000 hours and 2000 hours) using the CIE illuminant D65 and 10° colorimetric standard observer. Colorimetric measurements were made on the same area of each paint using a mask and a portable spectrophotometer (Data Color International). The optical system of the measuring head of the portable colorimeter uses diffuse illumination from a pulsed Xenon arc lamp over an 8 mm-diameter measuring area, with a 0° viewing angle geometry (see Appendix 3, p.129, for further details). The CIEDE2000 ( $\Delta E_{00}$ ) colour space was used to calculate colour differences. The visual and molecular changes which resulted were observed through colorimetry,  $\mu$ FTIR,  $\mu$ spectrofluorimetry, FORS, microfading spectrometry and Vis-NIR reflectance hyperspectral imaging.

Two main difficulties were encountered throughout the accelerated light ageing experience. To start with, the paint films did not adhere well to the glass slides and were not completely homogenous resulting in some areas in which the paint was more concentrated than others. The second issue was related to the brittleness of paints which resulted in the loss of paint during the experience due to the ventilation inside the solarbox. The visual results of the aging experience are shown in **Figure 33**.

**Table 17.** Identification of the 15 glass slides included in the accelerated light ageing experience, the respective pigments and binders.

| Glass Slide | Pigment*   | Binder     | Glass Slide | Pigment* | Binder |
|-------------|------------|------------|-------------|----------|--------|
| –           | FOC W&N    | Gum-arabic | 8           | FOC      | PVAc   |
| =           | FPC W&N    |            | 9           | FPC      |        |
| ≡           | Purple W&N |            | 10          | Scarlet  |        |
| 1           | CrimCa     |            | 11          | CrimCa   |        |
| 2           | FOC        |            | 12          | CrimAl   |        |
| 3           | CrimAl     |            | 13          | Purple   |        |
| 4           | Purple     |            |             |          |        |
| 5           | Scarlet    |            |             |          |        |
| 6           | FPC        |            |             |          |        |

\* Composition of pigments:

CrimCa: FPC dispersion, gypsum

FOC: Citric acid, milk, sodium borate, alum

CrimAl: FPC dispersion, aluminate

Purple: Citric acid, potassium carbonate, cream of tartar, alum, zinc sulphate

Scarlet: FPC dispersion, aluminate, vermilion

FPC: Potassium carbonate, alum, cream of tartar, calcium carbonate

<sup>40</sup> In the CIE  $L^* a^* b^*$  colour space system, the  $L^*$  is the lightness variable ( $L^* = 0$  is black,  $L^* = 100$  is white), and the chromaticity coordinates are represented by  $a^*$  ( $a^*$  means redness,  $-a^*$  means greenness) and  $b^*$  ( $b^*$  means yellowness,  $-b^*$  means blueness) (Schanda 2007).

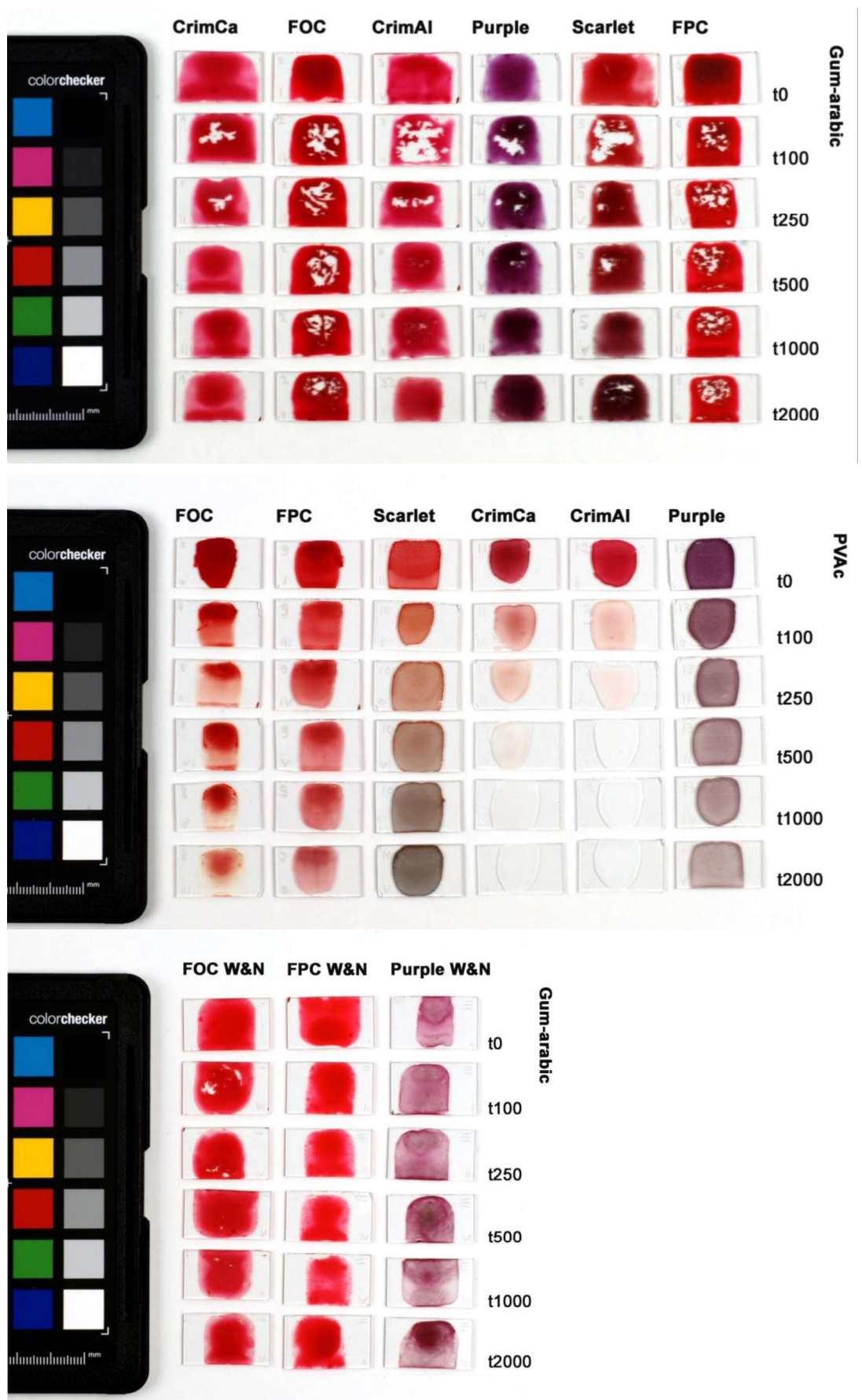


**Figure 33.** Paints prepared with reconstructions and historical samples of cochineal pigments subjected to the accelerated light ageing experience.

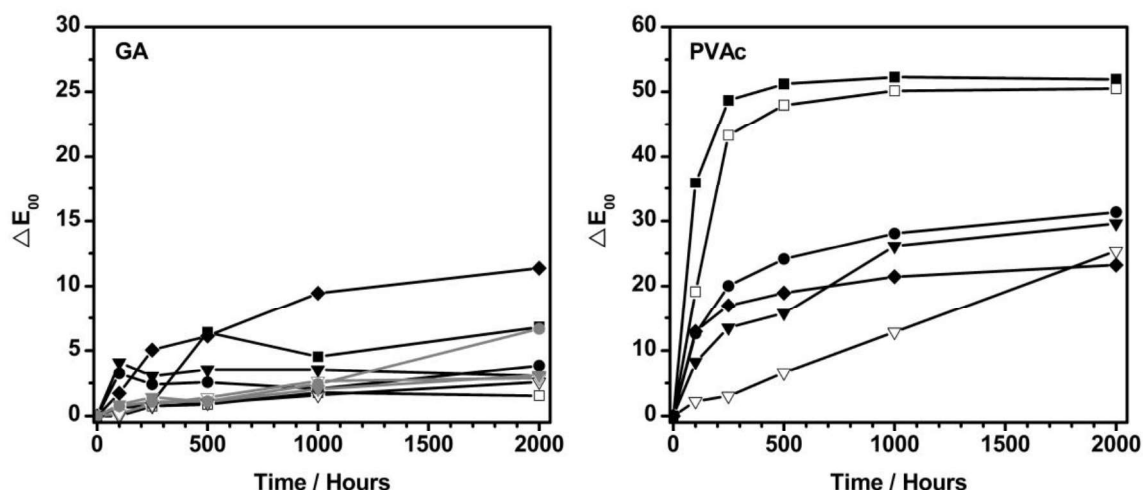


**Figure 34.** Colour differences obtained for cochineal paints with gum-arabic and PVAc after 2000 hours of exposure in the solarbox ( $\lambda_{irr} > 320$  nm): Scarlet (◆), CrimGyp (□), CrimAl (■), Purple (●), FOC (▽), FPC (▼), Purple W&N (●), FOC W&N (▽), FPC W&N (▼).

Overall, the artificial light aging resulted in a greater colour change in the PVAc paints than in the gum-arabic paints which appear to offer some protection from colour change, **Table 18** and **Figure 34**. One possible explanation for this difference between PVAc and gum-arabic paints may be the fact that GA absorbs more at  $\lambda > 320$  nm, **Figure 35**, and consequently retains energy which will not be absorbed by the pigment, acting as protection against photodegradation.

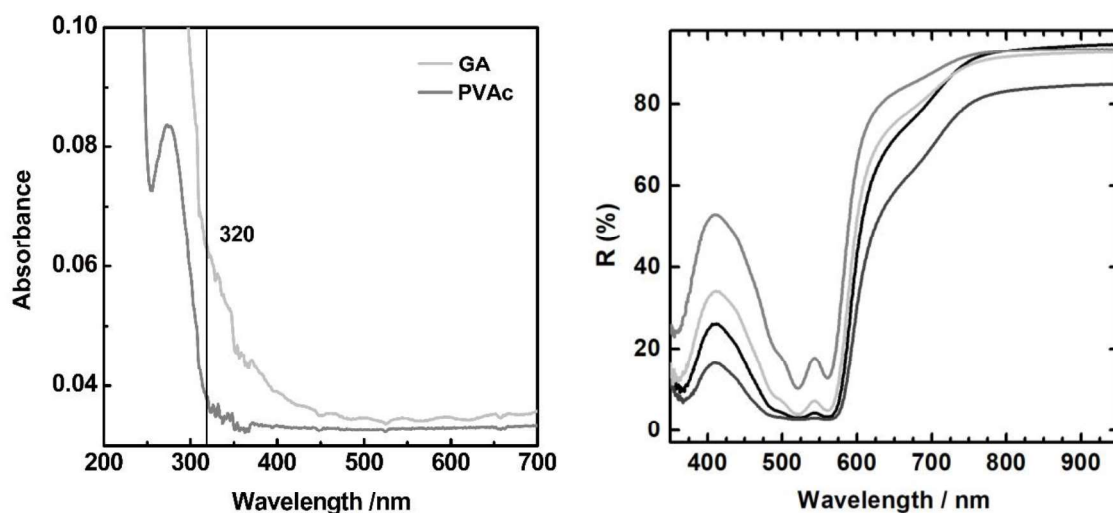


**Figure 35.** (Left) Absorbance spectra of gum-arabic and PVAc. (Right) Reflectance spectra of gum-arabic paint prepared with CrimCa at t 0 acquired in different areas of the same sample.

**Table 18.** L\* a\* b\* colour coordinates and respective colour differences ( $\Delta E_{00}$ ) of the paints exposed to irradiation.\*

| Binder     | Pigment    | t <sub>irr</sub> /h | L*         | a*         | b*         | $\Delta E_{00}$ |
|------------|------------|---------------------|------------|------------|------------|-----------------|
| PVAc       | CrimAl     | 0                   | 35.3 ± 0.1 | 47.3 ± 0.1 | 4.8 ± 0.1  |                 |
|            |            | 2000                | 86.7 ± 0.1 | -0.3 ± 0.1 | 2.7 ± 0.1  | <b>51.9</b>     |
|            | CrimCa     | 0                   | 34.0 ± 0.1 | 33.3 ± 0.1 | 3.4 ± 0.1  |                 |
|            |            | 2000                | 83.4 ± 0.1 | -0.2 ± 0.1 | 3.3 ± 0.1  | <b>50.5</b>     |
|            | Purple     | 0                   | 39.0 ± 0.1 | 15.2 ± 0.1 | -7.9 ± 0.1 |                 |
|            |            | 2000                | 68.2 ± 0.1 | 3.9 ± 0.1  | 4.2 ± 0.1  | <b>31.3</b>     |
|            | FPC        | 0                   | 34.8 ± 0.2 | 45.9 ± 0.3 | 19.0 ± 0.1 |                 |
|            |            | 2000                | 62.4 ± 0.9 | 19.8 ± 0.5 | 7.1 ± 0.2  | <b>29.6</b>     |
|            | FOC        | 0                   | 31.2 ± 0.1 | 44.9 ± 0.1 | 19.3 ± 0.1 |                 |
|            |            | 2000                | 57.1 ± 0.7 | 26.3 ± 0.8 | 16.6 ± 0.1 | <b>25.4</b>     |
|            | Scarlet    | 0                   | 43.7 ± 0.1 | 41.2 ± 0.2 | 13.7 ± 0.1 |                 |
|            |            | 2000                | 53.6 ± 0.2 | 3.2 ± 0.1  | 4.7 ± 0.1  | <b>23.2</b>     |
| Gum-arabic | Scarlet    | 0                   | 31.0 ± 0.2 | 41.6 ± 0.1 | 18.0 ± 0.1 |                 |
|            |            | 2000                | 27.0 ± 0.1 | 20.5 ± 0.2 | 3.7 ± 0.1  | <b>11.4</b>     |
|            | CrimAl     | 0                   | 35.8 ± 0.2 | 48.9 ± 0.0 | 11.0 ± 0.3 |                 |
|            |            | 2000                | 42.7 ± 0.3 | 42.9 ± 0.3 | 5.8 ± 0.1  | <b>6.8</b>      |
|            | Purple W&N | 0                   | 27.5 ± 0.2 | 23.5 ± 0.3 | 1.7 ± 0.2  |                 |
|            |            | 2000                | 35.8 ± 0.4 | 21.6 ± 0.2 | 0.1 ± 0.1  | <b>6.7</b>      |
|            | Purple     | 0                   | 22.6 ± 0.1 | 17.8 ± 0.1 | -4.0 ± 0.1 |                 |
|            |            | 2000                | 25.8 ± 0.2 | 20.8 ± 0.1 | -0.5 ± 0.1 | <b>3.8</b>      |
|            | FPC W&N    | 0                   | 37.6 ± 0.3 | 50.9 ± 0.4 | 27.1 ± 0.1 |                 |
|            |            | 2000                | 35.9 ± 0.1 | 46.1 ± 0.1 | 21.2 ± 0.2 | <b>3.1</b>      |
|            | FPC        | 0                   | 34.6 ± 0.1 | 44.8 ± 0.3 | 20.4 ± 0.2 |                 |
|            |            | 2000                | 37.8 ± 0.6 | 47.5 ± 1.3 | 19.4 ± 1.1 | <b>3.0</b>      |
|            | FOC        | 0                   | 34.6 ± 0.2 | 47.5 ± 0.2 | 21.9 ± 0.2 |                 |
|            |            | 2000                | 35.0 ± 0.2 | 52.4 ± 0.4 | 19.5 ± 0.0 | <b>2.6</b>      |
|            | FOC W&N    | 0                   | 38.4 ± 0.1 | 51.4 ± 0.1 | 22.1 ± 0.1 |                 |
|            |            | 2000                | 37.7 ± 0.4 | 47.9 ± 0.2 | 16.3 ± 0.1 | <b>2.9</b>      |
|            | CrimCa     | 0                   | 38.1 ± 0.3 | 52.0 ± 0.4 | 9.6 ± 0.4  |                 |
|            |            | 2000                | 39.2 ± 0.2 | 50.2 ± 0.2 | 11.4 ± 0.2 | <b>1.5</b>      |

\* The colour coordinates were calculated using the CIE illuminant D65 and 10° colorimetric standard observer, and the CIEDE2000 colour space was used to calculate colour differences. The standard deviation values result from three measurements in different areas of the same sample.

The colour differences within the gum-arabic paints were the highest for the Scarlet ( $\Delta E_{00} = 11.4$ ) and lower for the FOC ( $\Delta E_{00} = 2.6$ ) and CrimCa ( $\Delta E_{00} = 1.5$ ), while for the PVAc paints, the colour difference was higher for the crimsons ( $\Delta E_{00} = 50.5$ ), which show visually an almost complete loss of colour, and smaller for FOC ( $\Delta E_{00} = 25.4$ ) and Scarlet ( $\Delta E_{00} = 23.2$ ). The latter, however, shows

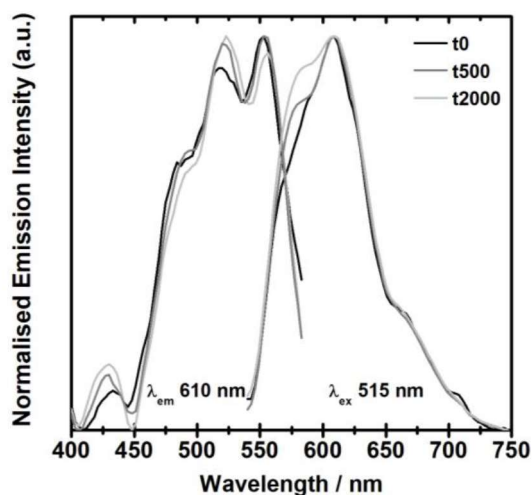


**Figure 36.** Excitation and emission spectra of CrimAl with gum-arabic subjected to the accelerated light ageing experience.

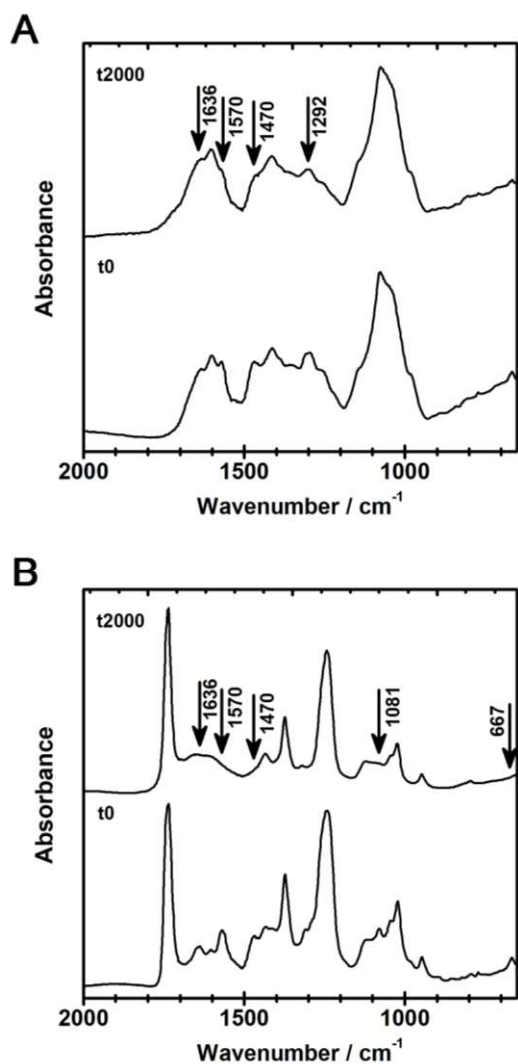


**Figure 37.** Infrared spectra of FOC with (A) gum-arabic and (B) PVAc before (t0) and after (t2000) the accelerated light ageing experience.

a very significant visual change in colour (see **Figure 33**). These results are somewhat surprising since it would be expected that the crimsons and scarlet, which have a higher amount of extender, would be less lightfast in both binders when compared with the carmines, which was not observed for CrimCa with GA and Scarlet with PVAc (Saunders and Kirby 1994a). The colour differences of the scarlet paints can be likely explained by the characteristic blackening of vermilion (Berrie and Strumfels 2017 and references cited therein; Miliani et al. 2018). Curiously, the Purple with PVAc showed a colour difference lower than that observed for the crimsons with PVAc, which is in agreement with the report that purple lakes were more durable than crimson lakes (p.16, Subchapter 1.2.2, and Carlyle 2001, p.502). Regarding the individual colour coordinates, overall, there was an increase in the  $L^*$  coordinate (i.e. an increase in lightness) and a decrease in the  $a^*$  (i.e. a decrease in the red component). A decrease in the  $b^*$  coordinate, indicating a decrease in the yellow component, was also observed for the majority of paints with the exception of the Purple with PVAc.

The analysis of results with FORS was particularly demanding since different areas in the same glass slide would result in different spectra depending on the saturation of the paint, **Figure 35**, making it difficult to understand if the spectral variation between different glass slides was due to the ageing of the paint or to the saturation of the paint (see **Figures 53-57**, Appendix 6, pp.145-149). With this respect, the application of reflectance hyperspectral imaging turned out to be a major advantage, as discussed in Subchapter 4.4, pp.78-86. Similarly,

µspectrofluorimetry results were inconclusive due to the low signal obtained. One exception was found for CrimAl with gum-arabic, which excitation and emission spectra are presented in **Figure 36**. The emission spectra, with maxima at 610 nm, shows the appearance of a shoulder/band at 583 nm while going from t0 to t2000 indicating the formation of a different emitting species.

µFTIR analysis showed a loss of colorant for FOC paints as observed by the decrease of the bands associated with the pigment in **Figure 37**. The µFTIR results obtained for the other paints (see **Figures 58** and **59**, Appendix 7, pp.150,151) were less conclusive due to the high influence of the binder which masks the signal of the pigment.<sup>41</sup>

## 4.2. Microfading spectrometry

Microfading spectrometry was developed by Whitmore and co-workers in the late 1990s to test the lightfastness of a colorant, i.e. its chemical stability after exposure to light, directly on artworks (Whitmore, Pan, and Bailie 1999). The application of this method is based on the “law of reciprocity” of light exposure which was postulated in the mid-19th century by Bunsen and Roscoe for simple photochemical reactions. This law states that ‘the net photochemical effect is the result of the total exposure which an object receives, which is the product of the light-sensitivity multiplied by the time’ (Bacci et al. 2004). In other words, it is the assumption that the intensity of light is inversely proportional to the time of exposure and that colorants fade to the same degree independently of the rate in which they are faded, e. g. 100 lux of intensity for 1 hour is considered to produce as much damage as 1 lux of the same radiation for 100 hours (Feller 1994). This assumption validates to a large extent all accelerated light ageing methods since it relates the exposure doses obtained from artificial ageing to those typically found in a museum environment (Ford 2011; Łojewski et al. 2011; Hoyo-Meléndez and Mecklenburg 2011).

A microfading tester, also called microfadometer, makes in situ real-time measurements of colour using visible reflectance spectroscopy upon exposure to a light so intense that it is capable of fading fugitive materials in a relatively short period of time, therefore indicating the tendency of the colour to change. The principle of this method is to focus a submillimetre uniform area - usually between 0.2 and 0.5 mm - of very intense visible light on a colorant using an optical fibre. Most microfading testers use a 75 W xenon light source with filters. The illuminance on the test area can vary between 1 and 16 megalux (Mlx), as opposed to the low illuminations, e.g. 50-250 lux, generally found in museums (Prestel 2017). A second optical fibre directs the collected reflected light to a spectrophotometer allowing to record the resulting colour changes. The two fibres, which provide non-contact measurement and detection, are held in a 0°/45° geometry, with the illumination beam

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<sup>41</sup> Gum-arabic can be characterised in the infrared region by a broad band centred at 3380 cm<sup>-1</sup> resulting from the OH stretching and by the glycoside bonds that present skeletal C-O and C-C vibration bands in the region 1200-1000 cm<sup>-1</sup> (ν(COC) at 1150 cm<sup>-1</sup>, ν(CC(CO)) at 1120 and 1040 cm<sup>-1</sup>, and δ(OH) and ν(CO) at 1080 cm<sup>-1</sup>) (Synytsya et al. 2003). PVAc presents the following infrared characteristics bands: ν(CH) at 2972 and 2924 cm<sup>-1</sup>, ν(C=O) at 1730 cm<sup>-1</sup>, δ(CH<sub>2</sub>) at 1435 cm<sup>-1</sup>, δ(CH<sub>3</sub>) at 1372 cm<sup>-1</sup> and ν(C=O-O-C) at 1233 and 1021 cm<sup>-1</sup> (Ferreira 2011).

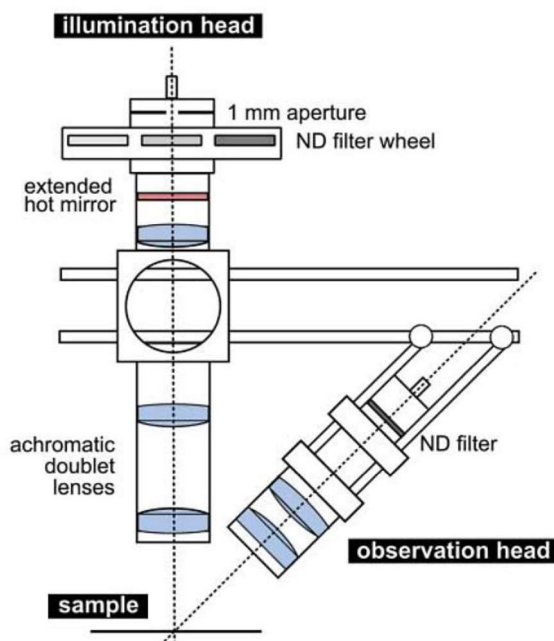


**Figure 38.** General schmatic of the arrangement of the optical componetes of a microfadometer. Figure from Łojewski et al. 2011.

oriented normal to the test area and the reflected light gathered at 45° from the normal. This configuration, **Figure 38**, allows for analysis of the diffusely reflected light from the test area, which contains information about the colour of the material. If the colorant is prone to fading, the exposure to light will cause the reflectance spectrum to change, being possible to stop it at any time. Even though the choice of the level of colour change that is to be considered an endpoint to the test is arbitrary, it is usually selected to be large enough to be easily measurable by the spectrophotometer but not so large as to produce a visually perceptible change. Filters and hot mirrors are commonly part of the microfading tester to remove ultraviolet (UV) and infrared radiation,

therefore ensuring that the spectrum of illumination is formed by visible light only. Most museums use filters to block UV radiation since it is not needed to view artworks and often causes more damage than visible light (Lerwill, Brookes, et al. 2015). In this sense, the removal of UV radiation in the microfading testers simulates a museum environment, while the removal of infrared radiation aims at reducing the temperature in the test area.

Spectral changes that occur during a microfading test, which usually takes from 10 minutes to half an hour, are converted into the International Commission on Illumination (Commission Internationale de l'Eclairage, CIE)  $L^* a^* b^*$  colour coordinates commonly using the D65 standard illuminant and 2° colorimetric standard observer. Standard illuminants, i.e. light sources, are used in colorimetry to calculate the tristimulus XYZ values of reflected colours under specified conditions of illumination (Hoyo-Meléndez et al. 2015). The D65 is a standard illuminant that represents average daylight illumination with a colour temperature of 6500 K (Johnston-Feller 2001). In addition, since the tristimulus values depend on the observer's field of view, the CIE established a colorimetric standard observer which represents the chromatic response of an average person within a 2° or 10° arc inside the fovea. The 2° is the angle that contains the largest concentration of colour-sensitive cones (Hoyo-Meléndez et al. 2015). An observer with this angle corresponds to the observation of an object with a small size (using an optical instrument), while an observer with the angle of 10° corresponds to the observation of an object in normal conditions (Mokrzycki and Tatol 2012). Once calculated, the CIE  $L^* a^* b^*$  colour coordinates are then used to calculate the colour difference, i.e. the amount of colour change,  $\Delta E$ , using the CIELAB ( $\Delta E_{ab}$ , also called  $\Delta E_{76}$ ) or CIEDE2000 ( $\Delta E_{00}$ ) formulas. The former is the most traditional colour space, still commonly used within the cultural

heritage field, although it is perceptually less uniform, which means that a  $\Delta E_{76}$  value might be perceptible for some colours, but not for others (Liang et al. 2011). On the other hand, changes recorded with the more sophisticated CIEDE2000 formula, the most perceptually uniform colour space published by the CIE in 2001, show closer resemblances to those perceived by the human eye (Luo, Cui, and Rigg 2001; Sharma, Wu, and Dalal 2005; Hoyo-Meléndez, Świt, and Sobczyk 2018). Although the colour difference is the main parameter discussed regarding microfading tests, the  $L^* a^* b^*$  colour coordinates can also be analysed to give a more detailed description of how the colour has changed. This is particularly important in cases in which the colour does not fade in the conventional sense, i.e. increasing in lightness towards white, but instead changes hue (Morris and Whitmore 2007).

The amount and rate of colour difference of a colorant measured with microfading spectrometry is usually compared to the fading of reference standards which are tested with the microfading tester under the same experimental conditions. The Blue Wool (BW) standards are photosensitive materials developed by the German Colour Fastness Committee (Deutsche Echtheitskommission) which were introduced in the field of cultural heritage in the 1950s and are considered nowadays the only reasonable reference material for evaluating the lightfastness of colorants (Hoyo-Meléndez and Mecklenburg 2011; Hoyo-Meléndez, Świt, and Sobczyk 2018). They consist of a reference set of eight blue-dyed wool cloths attached to a white cardboard substrate which present increasing lightfastness by a factor of two, relative to the previous one, and fade at different rates when exposed to light (Bacci et al. 2004; Hoyo-Meléndez and Mecklenburg 2011). BW1 is the most light-sensitive reference, while BW8 is the most lightfast. In microfading tests, usually only the three most light-sensitive standards BW1-BW3 are used since they include the range of colorants described as having high sensitivity to light in museum environments. Colorants more lightfast than these are out of the sensitivity range of microfading spectrometry and are not at serious risk of fading under normal museum lighting conditions (Ford and Druzik 2013; Hoyo-Meléndez et al. 2016; Prestel 2017). According to Hoyo-Meléndez et al. 2016, a typical light-sensitivity scale used is BW1: very high, BW2: high, and BW3: moderate.

Microfading spectrometry has been used in numerous cultural heritage institutions to evaluate the lightfastness of sensitive colorants in their collections (Hoyo-Meléndez, Świt, and Sobczyk 2018). For example, Ford 2011; Hoyo-Meléndez and Mecklenburg 2010; Mecklenburg and Hoyo-Meléndez 2012; Hoyo-Meléndez and Mecklenburg 2012; Hoyo-Meléndez et al. 2015; Lerwill, Townsend, et al. 2015; Stenger et al. 2016; Troalen et al. 2016; Soleymani, Ireland, and McNevin 2016; Lowe et al. 2017; Smith et al. 2018; Hoyo-Meléndez, Świt, and Sobczyk 2018. Moreover, Lerwill et al. 2008 constructed a microfading tester to which a linear variable filter system was added, enabling to assess the wavelength dependence of fading.

The usefulness of the microfading method is related to the possibility to make in situ measurements, avoiding the use of reference materials that usually do not exactly replicate real artworks with their complex compositions and histories. The damage caused to the artwork itself - unnoticeable by the average person - is minimum due to the small size of the test area which is necessary to achieve high intensities. Moreover, the fact that the exact same area is measured



**Figure 39.** Microfading testing on a cochineal paint: the size of the illuminated test area is about 0.5 mm in diameter.

throughout the test minimises possible measurement errors and the testing times are relatively short when compared to other accelerated light ageing methods. There are, however, some possible drawbacks associated such as the almost negligible size of the test area which may not be representative of the entire area in terms of colour and texture. Consequently, the resulting colour changes may under or overestimate the amount of colour difference that can occur for the entire area. For example, if the colour area is perceived as an additive mixture of small coloured areas, the changes measured on small areas of colour may not

translate accurately to the changes in appearance of the material (Whitmore, Bailie, and Connors 2000). Not only that, the megalux levels required to shorten test times may increase the probability and extent of “reciprocity failure”, i.e., deviations from the reciprocity law. The reciprocity failure is used when the fading under high intensities does not resemble the outcome of exposure to the same dose of lower intensity and is usually common for materials with high sensitivity to light (Hoyo-Meléndez and Mecklenburg 2011; Ford and Druzik 2013). In these cases, failure has been attributed to some condition that occurs under exposure to high light intensities and not under low intensities (Whitmore, Bailie, and Connors 2000).

As a relatively new method, the development and acceptance of microfading spectrometry benefits from comparisons between microfading tests and conventional accelerated light ageing techniques to support the correct interpretation of the data obtained (Lowe et al. 2017). Whitmore, Pan, and Bailie 1999 have published data for a few colorants that illustrate equivalence between microfading and conventional light ageing. On the other hand, Mecklenburg and Hoyo-Meléndez 2012 state that discrepancies have been observed after comparing microfading testing results with those obtained using conventional accelerated ageing methods. Few other studies providing comparison between microfading data and conventional light-ageing data exist.

The microfading tester used at the Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects (LANBOZ) was designed and developed by researchers at the National Museum in Krakow and at the Faculty of Chemistry of the Jagiellonian University (Łojewski et al. 2011) and is based on the original prototype designed by (Whitmore, Pan, and Bailie 1999). This instrument consists of a high-power light source, a 0°/45° (illumination/collection) geometry optical setup with fibre optics and a visible reflectance spectrometer. The high-power light source used is an HPLS 30-04 solid state plasma light source (LIFI) from Thorlabs, New Jersey, USA ( $400 \leq \lambda_{irr} \leq 750$  nm). The size of the illuminated test area is about 0.5 mm in diameter, **Figure 39**. The intensity of illumination on the test area - 3.3 or 4.3 Mlx - was measured with an ELSEC 765C environmental monitor from Littlemore Scientific - ELSEC (United Kingdom). The temperature at the surface of the sample can increase up to 2 °C. The working distance measured from the external lens of the

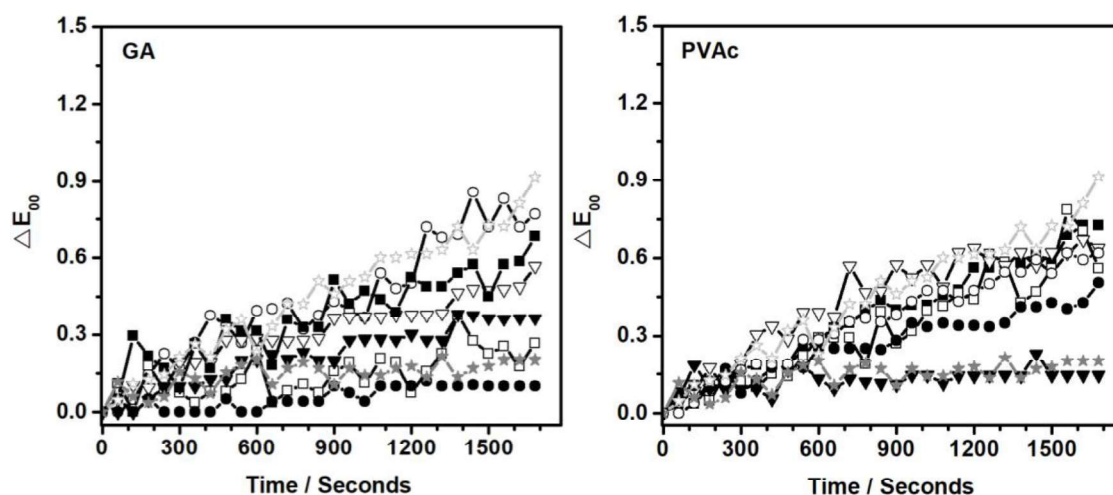


**Figure 40.** Microfading curves obtained for cochineal paints after 28-minute (1680 s) exposures to an illumination intensity of 3.3 Mlx. Scarlet (○), CrimCa (□), CrimAl (■), Purple (●), FOC (▽), FPC (▼), BW2 (★), BW3 (★).

illuminating probe to the surface of the sample is approximately 1 cm. The spectrometer used is an Ocean Optics (Florida, USA) Jaz miniature device with the SpectraSuite® spectrometer operating software.

The microfading tests were conducted in open-air under laboratory room conditions (temperature,  $T \approx 20\text{ }^{\circ}\text{C}$ ; relative humidity,  $RH \approx 56\%$ ) with the lights off. Before starting the tests, the intensity of the light source was checked on a Spectralon® white standard to avoid that the collected signal would saturate the spectrometer. The integration time used was 20 milliseconds and 10 acquisitions were averaged for each spectrum. A white reference spectrum and dark spectrum were then acquired. The white reference spectrum was recorded on the Spectralon® white standard while the dark spectrum was measured after placing a black cardboard in the optical path between the light source and the test area. To calculate the  $L^* a^* b^*$  colour coordinates, the CIE illuminant and colorimetric standard observer selected were D65 and 2 degree, respectively. The sample was placed underneath the vertical probe which is then adjusted to achieve best focus and acquire maximum reflected intensity on the test area. The first visible reflectance spectrum was used as reference and subsequent spectra were collected every 60 seconds for total testing times in the range 28-118 minutes. Colour differences were calculated using the initial spectrum as the basis for comparison. The CIELAB ( $\Delta E_{76}$ ) and CIEDE2000 ( $\Delta E_{00}$ ) colour spaces were both used. The glass slides were fixed onto a white board covered with a Teflon strip. Blue Wool standards BW1-BW3 were tested under the same conditions.

Microfading tests were carried out on the cochineal paints for 28 minutes (1680 seconds) at 3.3 Mlx, providing a total exposure of 1.54 Mlx·h. Colour coordinates  $L^* a^* b^*$  and colour differences calculated using both the CIELAB ( $\Delta E_{76}$ ) and CIEDE2000 ( $\Delta E_{00}$ ) colour spaces are presented in **Table 19**. **Figure 40** shows the microfading curves ( $\Delta E_{00}$  vs time) obtained (see **Figure 60**, Appendix 8, p.152, for individual microfading curves). Cochineal paints showing the highest  $\Delta E_{00}$  and appearing to fail to reach a stable rate of colour change after 28 minutes (CrimAl + GA, CrimAl +

PVAc, CrimCa + GA, Scarlet + GA, FOC + PVAc), were further tested on different areas of the same sample for 78 minutes (4680 seconds) at 3.3 Mlx, providing an exposure of 4.29 Mlx\*h, **Table 20**. For comparison, the colorimetric results obtained for blue wool standards BW1-BW3 tested under the same conditions as the cochineal paints are shown in **Table 21**. The microfading curves obtained for BW2 and BW3 are presented in **Figure 40**.

**Table 19.** Colour coordinates L\* a\* b\* and colour differences  $\Delta E_{76}$  and  $\Delta E_{00}$  for cochineal paints after 28-minute exposures to an illumination intensity of 3.3 Mlx.

|                       | Pigment Binder         | Time (min) | Exposure (Mlx*h) | L*   | a*   | b*    | $\Delta E_{76}$ | $\Delta E_{00}$ |
|-----------------------|------------------------|------------|------------------|------|------|-------|-----------------|-----------------|
| <b>Purple</b>         | Purple Lake            | 0          | 0                | 42.9 | 37.2 | -20.9 |                 |                 |
| <b>+ GA</b>           | Gum-arabic 10%         | 28         | 1.54             | 43.0 | 37.1 | -20.9 | 0.14            | 0.10            |
| <b>Purple W&amp;N</b> | Purple Lake W&N        | 0          | 0                | 29.6 | 23.1 | -2.8  |                 |                 |
| <b>+ GA</b>           | Gum-arabic 10%         | 28         | 1.54             | 29.6 | 23.1 | -2.6  | 0.20            | 0.13            |
| <b>FPC</b>            | Fine Printing Carmine  | 0          | 0                | 26.6 | 26.3 | 23.8  |                 |                 |
| <b>+ PVAc</b>         | PVAc 20%               | 28         | 1.54             | 26.6 | 26.6 | 23.9  | 0.32            | 0.15            |
| <b>FPC W&amp;N</b>    | F. P. Carmine W&N      | 0          | 0                | 29.8 | 56.6 | 54.3  |                 |                 |
| <b>+ GA</b>           | Gum-arabic 10%         | 28         | 1.54             | 29.9 | 56.6 | 53.5  | 0.81            | 0.35            |
| <b>FOC W&amp;N</b>    | F. O. Carmine W&N      | 0          | 0                | 35.1 | 56.4 | 12.0  |                 |                 |
| <b>+ GA</b>           | Gum-arabic 10%         | 28         | 1.54             | 35.3 | 56.3 | 12.6  | 0.64            | 0.35            |
| <b>FPC</b>            | Fine Printing Carmine  | 0          | 0                | 39.4 | 66.7 | 14.2  |                 |                 |
| <b>+ GA</b>           | Gum-arabic 10%         | 28         | 1.54             | 39.8 | 66.8 | 14.0  | 0.46            | 0.37            |
| <b>Purple</b>         | Purple Lake            | 0          | 0                | 32.6 | 13.5 | -4.9  |                 |                 |
| <b>+ PVAc</b>         | PVAc 20%               | 28         | 1.54             | 33.0 | 13.1 | -4.5  | 0.69            | 0.50            |
| <b>CrimCa</b>         | Crimson with Gypsum    | 0          | 0                | 34.3 | 27.8 | 8.2   |                 |                 |
| <b>+ PVAc</b>         | PVAc 20%               | 28         | 1.54             | 34.7 | 27.3 | 8.7   | 0.81            | 0.56            |
| <b>FOC</b>            | Finest Orient Carmine  | 0          | 0                | 41.5 | 57.8 | 7.8   |                 |                 |
| <b>+ GA</b>           | Gum-arabic 10%         | 28         | 1.54             | 42.1 | 57.2 | 7.8   | 0.85            | 0.57            |
| <b>Scarlet</b>        | Scarlet                | 0          | 0                | 40.7 | 43.1 | 21.2  |                 |                 |
| <b>+ PVAc</b>         | PVAc 20%               | 28         | 1.54             | 41.1 | 42.5 | 21.8  | 0.94            | 0.62            |
| <b>FOC</b>            | Finest Orient Carmine  | 0          | 0                | 25.7 | 47.2 | 30.3  |                 |                 |
| <b>+ PVAc</b>         | PVAc 20%               | 28         | 1.54             | 25.9 | 47.5 | 31.6  | 1.35            | 0.64            |
| <b>CrimAl</b>         | Crimson with Aluminate | 0          | 0                | 31.4 | 54.1 | 11.1  |                 |                 |
| <b>+ GA</b>           | Gum-arabic 10%         | 28         | 1.54             | 31.5 | 54.0 | 12.4  | 1.31            | 0.68            |
| <b>CrimAl</b>         | Crimson with Aluminate | 0          | 0                | 36.6 | 39.2 | 3.2   |                 |                 |
| <b>+ PVAc</b>         | PVAc 20%               | 28         | 1.54             | 37.1 | 38.3 | 4.0   | 1.30            | 0.73            |
| <b>Scarlet</b>        | Scarlet                | 0          | 0                | 26.9 | 37.4 | 27.5  |                 |                 |
| <b>+ GA</b>           | Gum-arabic 10%         | 28         | 1.54             | 26.6 | 37.2 | 28.7  | 1.25            | 0.77            |

To test the representativeness of measurements, samples CrimCa + GA and CrimAl + PVAc after 4.29 Mlx\*h were tested twice in different areas of the paints; in both cases, a discrepancy of  $\Delta E_{00}$  was observed (0.36 vs 0.68 and 1.51 vs 2.43, respectively). This fact may be explained, at

least in part, by the inhomogeneity of the paints since the initial  $L^*$   $a^*$   $b^*$  coordinates show small variations depending on the test area within the same sample. It should also be noted that the colour differences calculated using the CIELAB colour space were consistently higher than the  $\Delta E$  values resulting from the CIEDE2000 formula. This difference between  $\Delta E_{76}$  and  $\Delta E_{00}$  was proven to be greater when the colour difference is higher, e.g. the  $\Delta E_{76}$  and  $\Delta E_{00}$  values for BW3 after 4.29 Mlx\*h are 0.42 and 0.26, respectively, while the  $\Delta E_{76}$  and  $\Delta E_{00}$  values for BW1 after 4.29 Mlx\*h are 24.82 and 17.40, respectively. For discussion of results, below, only the  $\Delta E_{00}$  will be referred to.

Considering the 28-minute microfading tests, the colour differences obtained ranged between  $\Delta E_{00} = 0.1$  for the Purple pigment with gum-arabic and  $\Delta E_{00} = 0.77$  for the Scarlet pigment with gum-arabic. These values are inferior to  $\Delta E_{00} \geq 1.5$ , which has been estimated as the change capable of producing a just noticeable difference (JND), i.e. the minimum colour difference that can be detected by the average person (Prestel 2017; Hoyo-Meléndez, Świt, and Sobczyk 2018). The fading observed with the paints prepared with historical samples of Carmine and Purple pigments matched well the fading of the paints prepared with the respective reconstructions. The analysis of the colour coordinates reveals that, in general, there was an increase in  $L^*$  and  $b^*$ , and a decrease in  $a^*$ . No clear relation was found between the lightfastness of the samples and the binders used. Following the light-sensitivity scale presented by Hoyo-Meléndez et al. 2016, the Purple and Purple W&N pigments with gum-arabic, together with FPC + PVAc showed  $\Delta E_{00} < \text{BW3}$  and therefore can be rated as having a moderate sensitivity to light. The remaining paints showed  $\text{BW3} < \Delta E_{00} < \text{BW2}$ , being classified as colorants with a high sensitivity to light. Within this group of colorants with high sensitivity to light, the Crimson and Scarlet products were the least lightfast. Looking at their microfading curves, **Figure 40**, these paints appear to fail to reach a stable rate of colour change within the 28-minute tests.

**Table 20.** Colour coordinates  $L^*$   $a^*$   $b^*$  and colour differences  $\Delta E_{76}$  and  $\Delta E_{00}$  for cochineal paints after 78-minute exposures to an illumination intensity of 3.3 Mlx.

|                | Time<br>(min) | Exposure<br>(Mlx*h) | $L^*$ | $a^*$ | $b^*$ | $\Delta E_{76}$ | $\Delta E_{00}$ |
|----------------|---------------|---------------------|-------|-------|-------|-----------------|-----------------|
| <b>CrimAl</b>  | 0             | 0                   | 34.7  | 60.2  | 2.9   |                 |                 |
| <b>+ GA</b>    | 78            | 4.29                | 34.6  | 59.8  | 3.2   | 0.51            | 0.20            |
| <b>Scarlet</b> | 0             | 0                   | 38.4  | 31.2  | 2.7   |                 |                 |
| <b>+ GA</b>    | 78            | 4.29                | 38.6  | 30.7  | 2.8   | 0.55            | 0.29            |
| <b>FOC</b>     | 0             | 0                   | 31.3  | 46.5  | 26.8  |                 |                 |
| <b>+ PVAc</b>  | 78            | 4.29                | 31.9  | 46.5  | 26.9  | 0.61            | 0.48            |
| <b>CrimCa</b>  | 0             | 0                   | 25.9  | 54.3  | 33.9  |                 |                 |
| <b>+ GA</b>    | 78            | 4.29                | 26.0  | 54.5  | 33.3  | 0.64            | 0.36            |
|                | 0             | 0                   | 26.7  | 45.6  | 19.5  |                 |                 |
|                | 78            | 4.29                | 26.3  | 45.1  | 20.4  | 1.11            | 0.68            |
| <b>CrimAl</b>  | 0             | 0                   | 35.7  | 38.5  | 5.3   |                 |                 |
| <b>+ PVAc</b>  | 78            | 4.29                | 36.8  | 36.4  | 6.6   | 2.70            | 1.51            |
|                | 0             | 0                   | 36.1  | 38.7  | 4.5   |                 |                 |
|                | 78            | 4.29                | 35.9  | 36.5  | 8.1   | 4.22            | 2.43            |

**Table 21.** Colour coordinates L\* a\* b\* and colour differences  $\Delta E_{76}$  and  $\Delta E_{00}$  for blue wool standards BW1-BW3 after 28-minute and 78-minute exposures to an illumination intensity of 3.3Mlx.

|            | Time (min) | Exposure (Mlx*h) | L*   | a*   | b*    | $\Delta E_{76}$ | $\Delta E_{00}$ |
|------------|------------|------------------|------|------|-------|-----------------|-----------------|
| <b>BW3</b> | 0          | 0                | 43.3 | 8.9  | -48.5 |                 |                 |
|            | 28         | 1.54             | 43.2 | 9.4  | -49.0 | 0.71            | 0.20            |
|            | 78         | 4.29             | 43.2 | 9.3  | -48.6 | 0.42            | 0.26            |
| <b>BW2</b> | 0          | 0                | 40.1 | -2.7 | -46.7 |                 |                 |
|            | 28         | 1.54             | 39.2 | -2.5 | -45.5 | 1.51            | 0.91            |
|            | 78         | 4.29             | 38.3 | -3.3 | -43.3 | 3.89            | 1.74            |
| <b>BW1</b> | 0          | 0                | 35.1 | -1.9 | -31.4 |                 |                 |
|            | 28         | 1.54             | 17.3 | 0.9  | -29.3 | 18.14           | 13.50           |
|            | 78         | 4.29             | 10.9 | -2.5 | -25.9 | 24.82           | 17.40           |

**Table 22.** Colour coordinates L\* a\* b\* and colour differences  $\Delta E_{76}$  and  $\Delta E_{00}$  for cochineal paint after 28-minute and 118-minute exposures to an illumination intensity of 4.3 Mlx.

|               | Time (min) | Exposure (Mlx*h) | L*   | a*   | b*  | $\Delta E_{76}$ | $\Delta E_{00}$ |
|---------------|------------|------------------|------|------|-----|-----------------|-----------------|
| <b>CrimAl</b> | 0          | 0                | 37.8 | 39.1 | 8.7 |                 |                 |
| <b>+ PVAc</b> | 28         | 2.01             | 38.3 | 38.0 | 8.7 | 1.21            | 0.60            |
|               | 0          | 0                | 38.8 | 37.9 | 8.3 |                 |                 |
|               | 118        | 8.46             | 40.7 | 34.6 | 10  | 4.17            | 2.49            |

When tested for a longer period of time (78 minutes), the CrimAl and Scarlet pigments with gum-arabic and the FOC + PVAc showed lower colour differences when compared with the respective differences obtained after the 28-minute test but still staying within the BW2-BW3 range. The microfading curves, see **Figure 60**, Appendix 8, p.152, appear to have reached a stable rate of colour change. Higher colour changes ( $\Delta E_{00} = 1.51$ , BW2-BW3 range, and  $\Delta E_{00} = 2.43$ , BW1-BW2 range) were obtained with the CrimAl pigment with PVAc. In this case, the microfading curves still appear to fail to reach a stable rate. To produce an even larger colour change, this sample was tested for 28 and 118 minutes (7080 seconds) in different areas at 4.3 Mlx, providing an exposure of 2.01 and 8.46 Mlx\*h, respectively, **Table 22**. A  $\Delta E_{00} = 2.49$  was obtained after the exposure of 8.46 Mlx\*h (118-minute test at 4.3 Mlx) which is similar to the  $\Delta E_{00} = 2.43$  obtained after an exposure of 4.29 Mlx\*h (78-minute test at 3.3 Mlx). The microfading curve after the 118-minute exposure, see **Figure 61**, Appendix 8, p.153, indicates that higher  $\Delta E_{00}$  values would be obtained if the test would have kept going.

**Figure 41** presents the initial and final reflectance spectra of CrimAl + PVAc after exposures to 1.54 Mlx\*h (28-minute test at 3.3 Mlx,  $\Delta E_{00} = 0.73$ ), 4.29 Mlx\*h (78-minute test at 3.3 Mlx,  $\Delta E_{00} = 2.43$ ) and 8.46 Mlx\*h (118-minute test at 4.3 Mlx,  $\Delta E_{00} = 2.49$ ). While  $\Delta E_{00} = 0.73$  indicates a very small decrease in reflectance in the higher energy range of the visible spectrum, the  $\Delta E_{00}$  of 2.43

and 2.49 represent different spectral changes. This indicates that similar values of colour changes do not necessarily indicate the same spectral behaviour. Not only that, it also reveals that higher illumination intensities may cause different fading patterns or that the same paint, if applied in an inhomogeneous way, may present different fading behaviours.

### 4.3. Comparison between accelerated light ageing with a solarbox and microfading spectrometry

Differences were found after comparing the microfading testing results with those obtained with the accelerated light ageing method using a solarbox equipped with a Xenon lamp ( $\lambda_{\text{irr}} > 320$  nm). As expected, due to the short irradiation times, the microfading tests produced smaller colour changes than those measured within the solarbox experiment. However, the relative lightfastness of the samples was also different. As shown in **Figure 34**, Subchapter 4.1, p.65, irradiation in the solarbox for 2000 hours resulted in a clear distinction between the light-sensitivity of the gum-arabic ( $1.5 \leq \Delta E_{00} \leq 11.4$ ) and PVAc ( $23.2 \leq \Delta E_{00} \leq 51.9$ ) paints, the latter being more unstable. While for the gum-arabic paints, the Scarlet pigment showed the higher colour difference, within the PVAc paints, the Crimson pigments were the most light-sensitive. In both cases, the Purple paints showed a considerable colour difference, contrary to what was

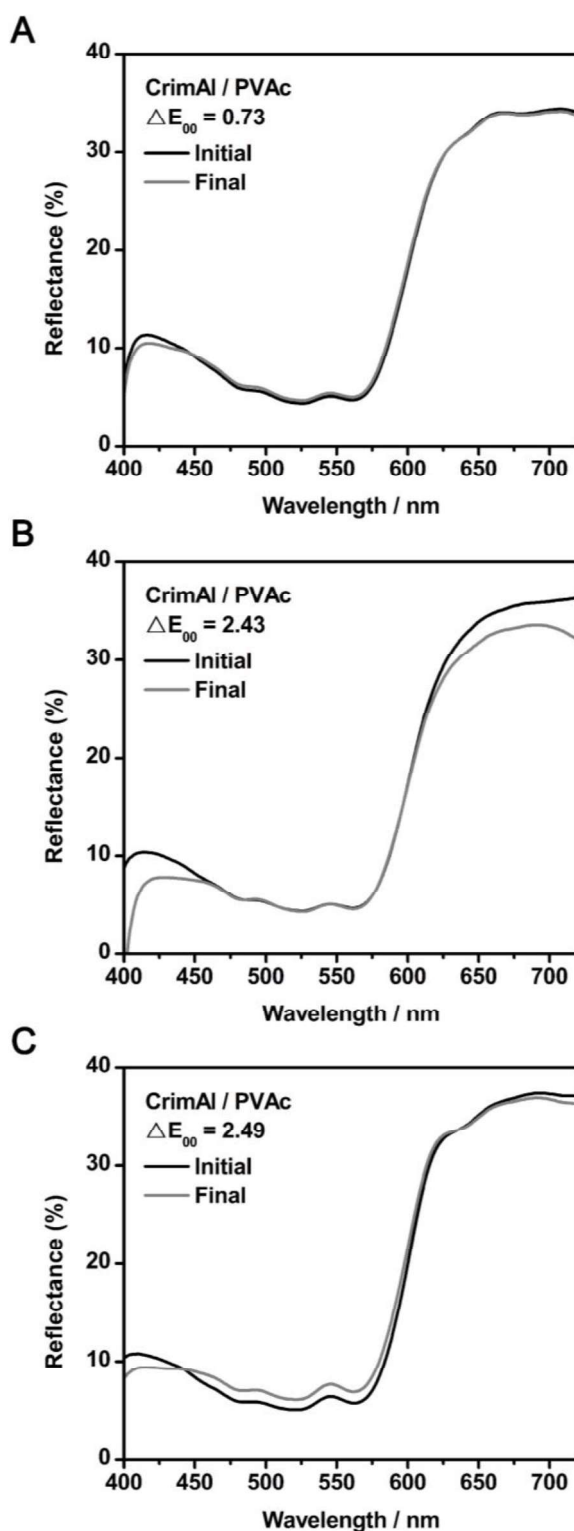


**Figure 41.** Initial and final reflectance spectra of CrimAl with PVAc after 28-minute exposure at (A) 3.3 Mlx (1.54 Mlx\*h), (B) 78-minute exposure at 3.3 Mlx (4.29 Mlx\*h), and (C) 118-minute exposure at 4.3 Mlx (8.46 Mlx\*h).

found with the microfading tests.

Several factors may account for the difference of results between both methods of accelerated light ageing. One of the most relevant reasons is the different light sources used and their spectral power distribution i.e. the relative amount of light energy at different wavelengths, **Figure 42**. It is known that colorants do not respond equally to all wavelengths and have greater sensitivity to certain regions of the electromagnetic spectrum. Since light sources may emit disproportionate amounts of radiation at wavelengths that can induce photodegradation in colorants absorbing those wavelengths, different spectral power distributions may cause distinct degrees of colour change (Saunders and Kirby 2001; Eng, Preusser, and Schaeffer 2016). This is generally more significant when the light source emits a higher proportion of UV radiation, recognized as a major contribution to degradation, however, it will affect colorants even when the ultraviolet is excluded. For example, it has been shown that while red and yellow lake pigments are more affected by blue visible light, the BW1 and BW2 standards, which reflect a higher proportion of these wavelengths, are more affected by light in the green/yellow region of the visible spectrum (Saunders and Kirby 1994b). In the present case, the presence of some part of UV radiation in the solarbox experience ( $\lambda_{irr} > 320$  nm) and its absence in the microfading testing may contribute to the differences of relative lightfastness obtained for the cochineal paints. Another factor possibly accounting for the difference of results between both methods is the temperature and relative humidity at which the samples were exposed to light since it has been shown that greater colour changes may occur at higher temperature (Saunders and Kirby 2001). Moreover, the size of the test areas, much smaller and focused in the case of microfading spectrometry, and the different measurement modes and instruments of the colour coordinates may also contribute to the discrepancies of results observed between both methods.

It is noteworthy that microfading spectrometry and the conventional accelerated light ageing method using a solarbox are two methods developed for different purposes. The former is intended to assess the relative lightfastness of colorants and to be applied on actual artworks without the

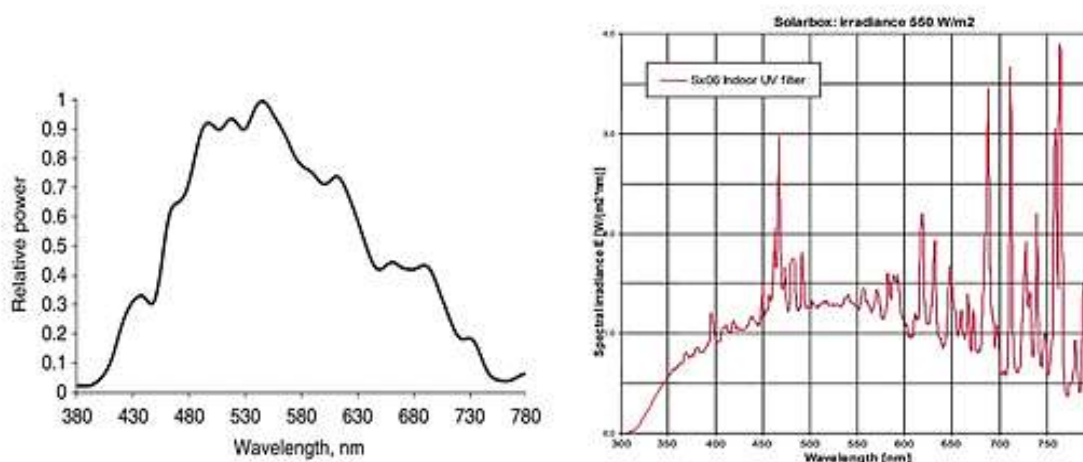


**Figure 42.** Spectral power distribution of (left) a HPLS 30-04 solid state plasma light source (from Hoyo-Meléndez, Świt, and Sobczyk 2018) and (right) a UV filtered xenon light source (from “Cofomegra Solarbox,” n.d.).

possibility of achieving high  $\Delta E_{00}$  values that can be visible to the naked eye, aiming to replicate an ageing in museum environments. The latter is a relatively more aggressive method which purpose is to cause higher changes to allow for the study of the mechanisms of photodegradation that may occur and the physical consequences thereof. In both cases, it is important to correctly interpret and contextualise the data obtained before extrapolating results to different contexts.

#### 4.4. Reflectance hyperspectral imaging in the Vis-NIR

In the past years, non-invasive reflectance spectroscopy in the ultraviolet, visible and near-infrared regions has played an increasingly important role in the scientific study of objects related to the cultural heritage (Bacci et al. 1991; Bacci and Picollo 1996; Leona and Winter 2001; Dupuis, Elias, and Simonot 2002; Bacci et al. 2003; Leona et al. 2004; Casini et al. 2005; Bacci et al. 2009; Appolonia et al. 2009; Aceto et al. 2012; Ricciardi, Pallipurath, and Rose 2013; Cucci, Bigazzi, and Picollo 2013; Muir et al. 2013; Melo et al. 2014; Aceto, Agostino, et al. 2014; Aceto et al. 2014; Cheilakou, Troullinos, and Kouli 2014; Delaney et al. 2014; Vetter and Schreiner 2014; Mounier and Daniel 2015). It is a well-established technique for the identification of coloured artists' materials, even though its low fingerprinting ability - when compared with molecular spectroscopic techniques such as Fourier transform infrared and Raman spectroscopies - prevents its reliable use as a self-consistent tool (Kubik 2007). On the other hand, due to considerable improvements in technology, interest has been focused on the development of imaging spectroscopy, which more and more has become accepted as a powerful technique for the scientific examination of cultural heritage objects, making it possible to obtain a large amount of spectroscopic information, as well as an accurate digital record of the object (Casini et al. 1999; Martinez et al. 2002; Fischer and Kakoulli 2006; Kubik 2007; Cucci et al. 2011a; Liang 2012). Reflectance imaging spectroscopy is a 2D spectroscopic technology based on the capture of sequences of images, almost contiguous, registered over spectral bands, over an extended spectral interval, typically covering the visible and/or the near infrared regions. This technology, initially developed in the 80s for remote sensing applications (Aikio 2001, p.23), started to be transferred into the cultural heritage field in the 2000s. In its most advanced approach, by using hyperspectral imaging devices (as opposed to multispectral, MSI), reflectance hyperspectral imaging (HSI) involves the acquisition of spatially co-registered images in hundreds of narrow spectral bands (bandwidth of few nanometres) in order to extract a spectrum at each point in the spectral image set (Cucci, Delaney, and Picollo 2016), **Figure 43**.<sup>42</sup> In the case of HSI in the UV-Vis-NIR regions, the spectral features collected relate to the electronic transitions and vibrational modes of the materials (Ricciardi and Delaney 2011).

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<sup>42</sup> Reflectance imaging spectroscopy is normally classified as either multispectral (MSI) or hyperspectral (HSI) which differ by the number of bands, their width and continuity. However, the definitions of MSI and HSI are very author-dependent. MSI systems acquire images over a limited number of spectral bands, usually with a set of filters having bandwidths from tens to hundreds of nanometres. HSI systems acquire images in narrower and more numerous contiguous bands, typically one hundred or more having bandwidths with < 10 nm. The advantage of HSI systems is to provide almost continuous spectral measurement. (George et al. 2017)

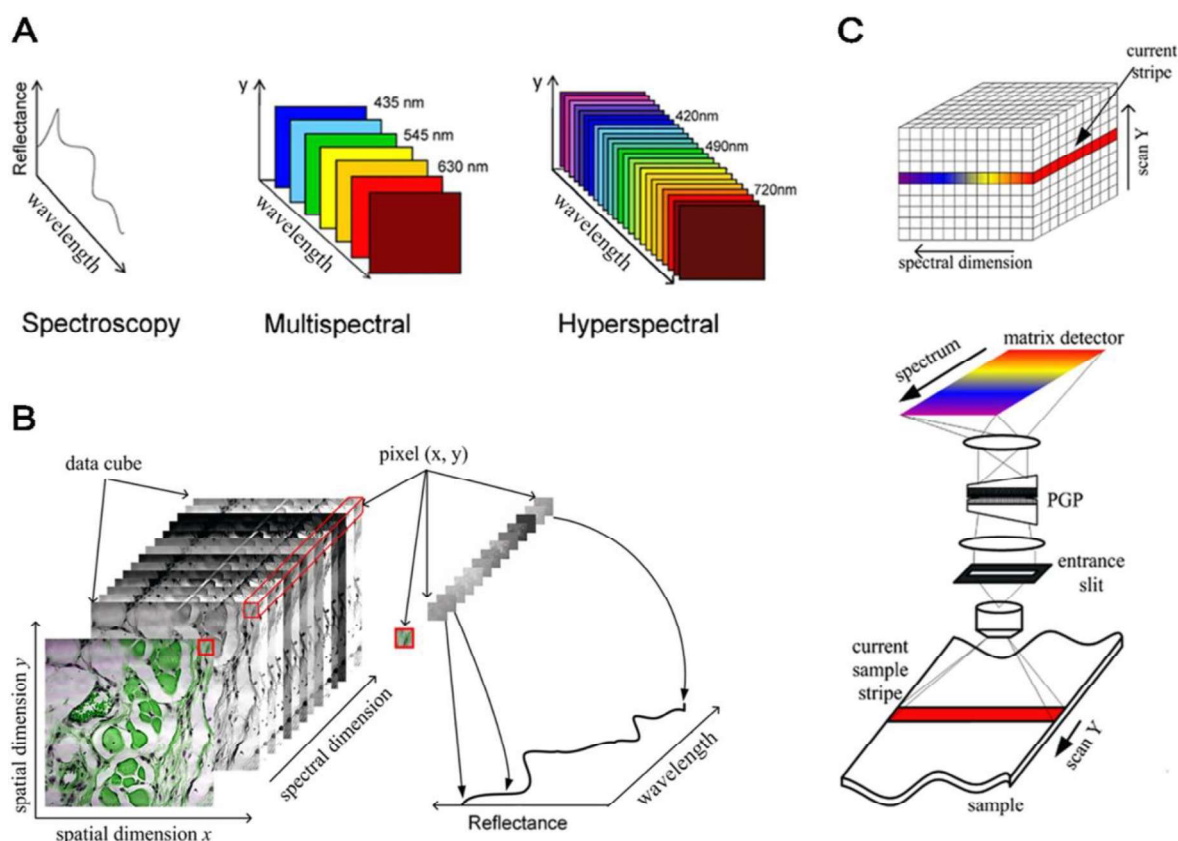


**Figure 43.** (A) Schematic comparison between spectroscopy, multispectral and hyperspectral. (B) The concept of a data cube, in which the cube face is a function of the spatial coordinates  $x$  and  $y$ , and the depth is a function of wavelength  $\lambda$ . (C) Push-broom spectral imaging approach. Figure adapted from Li et al. 2013.

The data-set acquired, called cube file or data cube, which is the complete dataset formed by the three dimensions - two spatial,  $x$  and  $y$ , and one spectral,  $\lambda$  - over which data is collected, **Figure 43**, provides a highly resolved reflectance spectrum over the investigated spectral range per each spatial pixel (picture element) of the imaged area, and can be suitably processed to obtain a non-invasive identification of materials and map their distributions throughout the surface. Along with the identification of many materials distributed over the painted surface, HSI data in the visible range allow calculation of colourimetric coordinates per each pixel of the imaged area, thus providing high-resolution colour (RGB) reproductions. Moreover, by means of appropriate algorithms, including multivariate analysis (such as Principal Component Analysis), the data cube may be processed to extract elaborated false colour maps, perfectly superimposable to the visible (e.g. RGB) image. This makes easier the interpretation of the spectroscopic data, helps to visualise hidden characteristics and details not detectable in the visible image, such as underdrawings, retouches, etc., and greatly enriches the readability of the artwork.

Even though spectral imaging techniques have been becoming more and more one of the tools used by the heritage community for the scientific study and documentation of artworks and artists' materials (Delaney et al. 2010; Ricciardi et al. 2012; Liang 2012; Ricciardi et al. 2013; Rosi et al. 2013; Cucci et al. 2013; Dooley et al. 2013; Mounier et al. 2014; Mounier and Daniel 2015; Delaney et al. 2016; Chlebda et al. 2016; Daniel et al. 2016; Dooley et al. 2017; Centeno et al. 2017;

Mulholland et al. 2017; Chlebda, Rogulska, and Łojewski 2017; Alfeld et al. 2018; Cucci et al. 2018; Viguerie et al. 2018; Cucci et al. 2019), their potentialities have been partially counteracted by the complexity and costs of instrumentation, the need of software and hardware resources to store and process the big-size data cubes and, also, the need of skilled professionals to make the final data fully exploitable. Various methods of multivariate analysis for data treatment have been proposed to support the processing and interpretation of the large amount of data acquired (Polak et al. 2017; Catelli et al. 2017; Pouyet et al. 2018; Bonifazi et al. 2019). In addition, in order to address all the conservation-related issues, several methods, with different systems and image processing capabilities have been developed (Saunders and Cupitt 1993; Saunders, Cupitt, and Padfield 2006; Fischer and Kakoulli 2006). For example, if the aim of the analysis is to reveal tiny details such as the craquelure on the surface of a painting, spatial resolution may have to be enhanced with respect to spectral resolution. However, for accurate identification of materials or for measuring colour changes, a high spectral resolution is also needed (Bonifazzi et al. 2008). The various devices are commonly categorised according to the portion of the data cube that is acquired in a single detector readout (Hagen et al. 2012; George et al. 2017). They can consist in cameras equipped with filtering systems for the optical selection of the wavelengths, or can be constituted by scanners equipped with dispersive systems for the selection of the spectral bands, such as push-broom spectrometers - also known as line scanning - that collect data with a 2D array detector at all wavelengths simultaneously for one spatial line of the object so that only one spatial dimension needs to be scanned to fill out the data cube (Li et al. 2013), **Figure 43**. Some devices can also be based on snap-shot imaging systems, which collect the entire 3D file-cube in a single integration period without scanning (Cucci et al. 2011a; Hagen et al. 2012).

Following previous work by the author, which validated and demonstrated the advantages of applying HSI to the study of lake pigments (Vitorino et al. 2014), the hyperspectral imaging technique was applied in this work to support the study of cochineal references subjected to the accelerated light ageing experience. Hyper-spectral imaging in the 400-900 nm range was performed using a push-broom instrument that was designed and assembled at IFAC-CNR (Casini et al. 2005; Picollo et al. 2007; Cucci et al. 2011b). The system is based on a prism-grating-prism (PGP) line-spectrograph ImSpector™ V10E (SpecIm Ltd, Oulu, Finland), with a 30 µm slit, which is connected to a high sensitivity CCD camera (Hamamatsu ORCA-ERG, Hamamatsu, Japan). The line-segment analysed is usually focused on the entrance slit of the spectrograph by means of a telecentric lens Opto-Engineering Srl (Mantova, Italy), which is normally used to limit distortion due to effects when the surface is not perfectly planar. The line-segment is illuminated by two Schott-Fostec fibre-optic line-lights equipped with focusing lenses that are fixed to the scan-head and symmetrically project their beams at angles of 45° with respect to the normal direction of the imaged surface (0°/2x45° observation/illumination geometry). Light is supplied by a 3200 K 150-Watt QTH-lamp. The spectrographic head is mounted on a mechanical system which allows movements along two orthogonal axes of a vertical plane. The mechanical system can scan a maximum area of about 100 cm x 100 cm with 20 vertical line-scan stripes. The system provides a spatial sampling of ~ 11 points/mm (~ 279 ppi) and a resolution of better than 2 lines/mm at 50% of contrast reduction. The

system's spectral sampling is about  $\sim 1.2$  nm and resolution is  $\sim 2.5$  nm at half maximum. Before any measurement set, the system is calibrated with a certified Spectralon® white standard generally used at IFAC-CNR, and the variations with time of the emission of the QTH lamp are compensated by means of frequent refreshing of calibration. The calibration Spectralon® standard is also used to convert the image cubes to reflectance factor. Moreover, reflectance spectra are normalised by dividing them with a reference spectrum of the reflectance target acquired under the same conditions. After measurements and before data treatment, calibration of the wavelength axis is performed with a holmium oxide wavelength calibration standard.

The application of IFAC-CNR's imaging system to support the interpretation of the results obtained from the accelerated light ageing experience turned out to be extremely useful due to the difficulties faced with throughout the experience and described above (see Subchapter 4.1, pp.62-68). The hyperspectral data were acquired by imaging the glass slides from the ageing experience from t0 (time of exposure = 0) to t2000 (time of exposure = 2000 hours). To carry out the scan, the glass slides were fixed onto a white board covered with a Teflon strip. From the resulting data cube, constituted by 400 reflectance images within the 400-900 nm range, using ENVI software it was possible to select ROIs (regions of interest) covering only the areas in the glass slides with paint and extract average reflectance spectra without the influence of the areas in which paint has become loose or is extremely thin. These spectra allowed to analyse the reflectance behaviour of the paints from t0 to t2000 thanks to the averaging of the spectral characteristics between the areas where paint was more and less concentrated, **Figures 44-46**. The standard deviation of the average spectra, presented in **Figures 62-64**, Appendix 9, pp.154-156, shows that the spectral variation within each ROI is mainly centred around 600 nm, with the exception of the purple paints, which is centred at 650 nm. The ROIs of the FOC, FPC, FPC W&N and CrimAl with gum-arabic show the higher standard deviation, explained by a higher spectral heterogeneity of the paint within the selected ROI, while the crimsons, Scarlet and Purple with PVAc present the lowest standard deviation. In addition, all standard deviation spectra present a relatively high signal in the 400-425 nm range, indicating that the highest variation in the reflectance spectra exists in the left end of the spectra. This can be explained by the high noise in the signal in that range, which is due to the very low sensitivity of the hyperspectral system below 425 nm.

Overall, with respect to the gum-arabic paints, **Figures 44 and 46**, the greatest change in reflectance spectra was observed for the Scarlet, which corresponds to the colorimetry results presented in Subchapter 4.1, pp.65-66. Regarding the spectra of the PVAc paints, **Figure 45**, their behaviour throughout the 2000 hours clearly translate the loss of colour visually observed (**Figure 33**, Subchapter 4.1, p.64).

Analysing each individual paint, the FOC and FPC with gum-arabic present a strong absorption with no visible characteristic sub-bands. The FOC paint, in particular, shows an almost perfect S shape. Both paints present an inflection point around 598-609 nm and their reflectance shows differences throughout the different irradiation times mostly in the range 625-725 nm. From 250 hours on, it is possible to observe sub-bands at 519-522 nm and 562-567 nm. The behaviour of FOC W&N and FPC W&N match well that of the respective reconstructions. With PVAc, both FOC

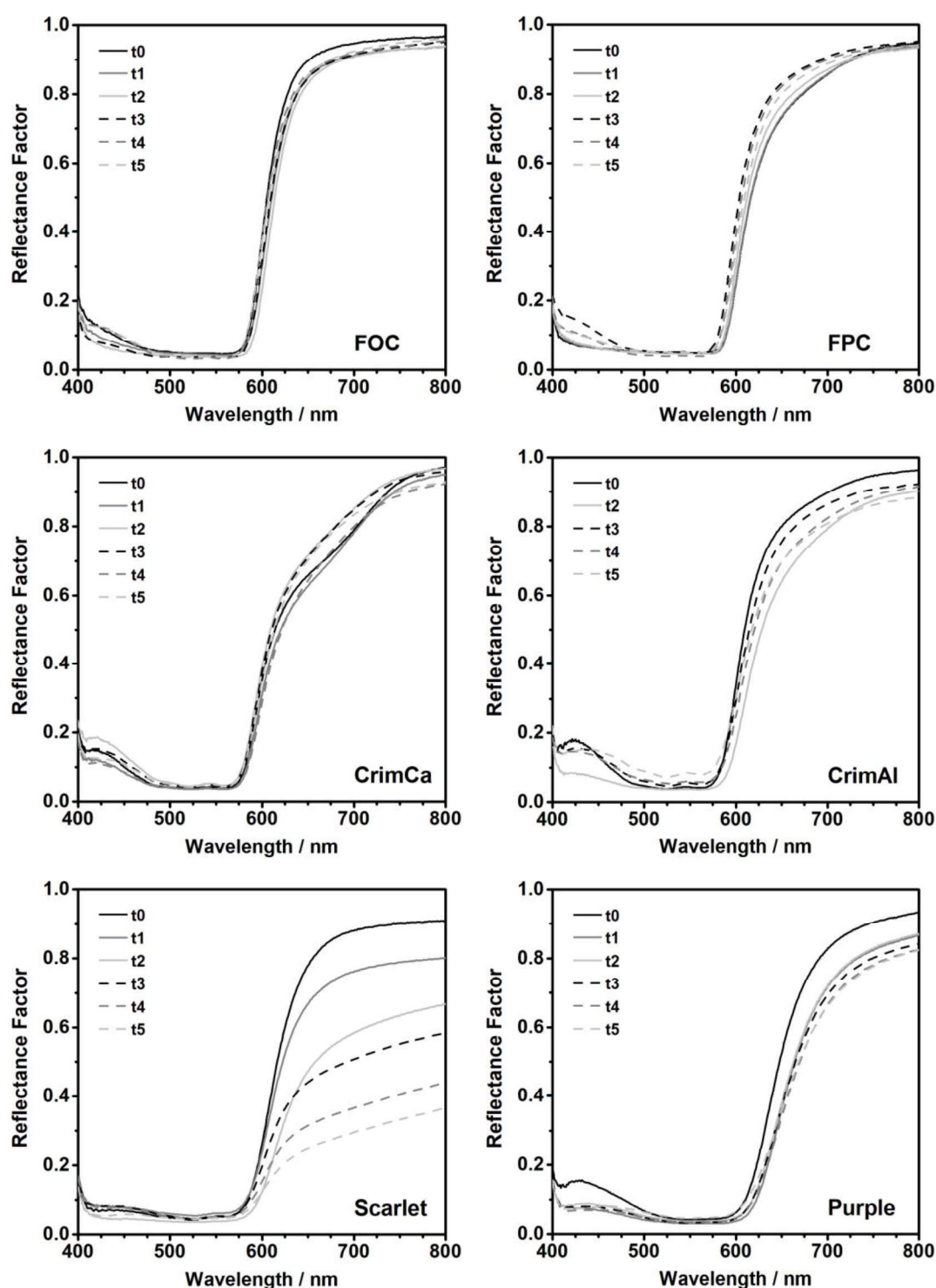


**Figure 44.** Reflectance average spectra extracted from ROIs of cochineal references with gum-arabic subjected to the accelerated light ageing experience.

and FPC show a clear difference from t0 to t2000, the sub-bands being easily observed at the end of the irradiation time.

CrimCa with gum-arabic shows two sub-bands at 520-522 nm and 560-561 nm and two inflection points at t0 and t100 which tend to disappear in the following times. The first inflection point appears at 588-592 nm and the second at 697-708 nm. The reflectance changes throughout the irradiation

time mostly in the range 625-725 nm. For the same pigment with PVAc, the inflection points appear only at t0 at 593-596 nm and 710 nm. In this case, the reflectance increases with the increase in the irradiation time. The two sub-bands at 520-523 nm and 557-561 nm are visible only until 250 hours. At t500, t1000 and t2000 the absorption is barely inexistent revealing an almost complete loss of colour. CrimAl shows a similar behaviour to that of CrimCa, while the Scarlet with both gum-arabic

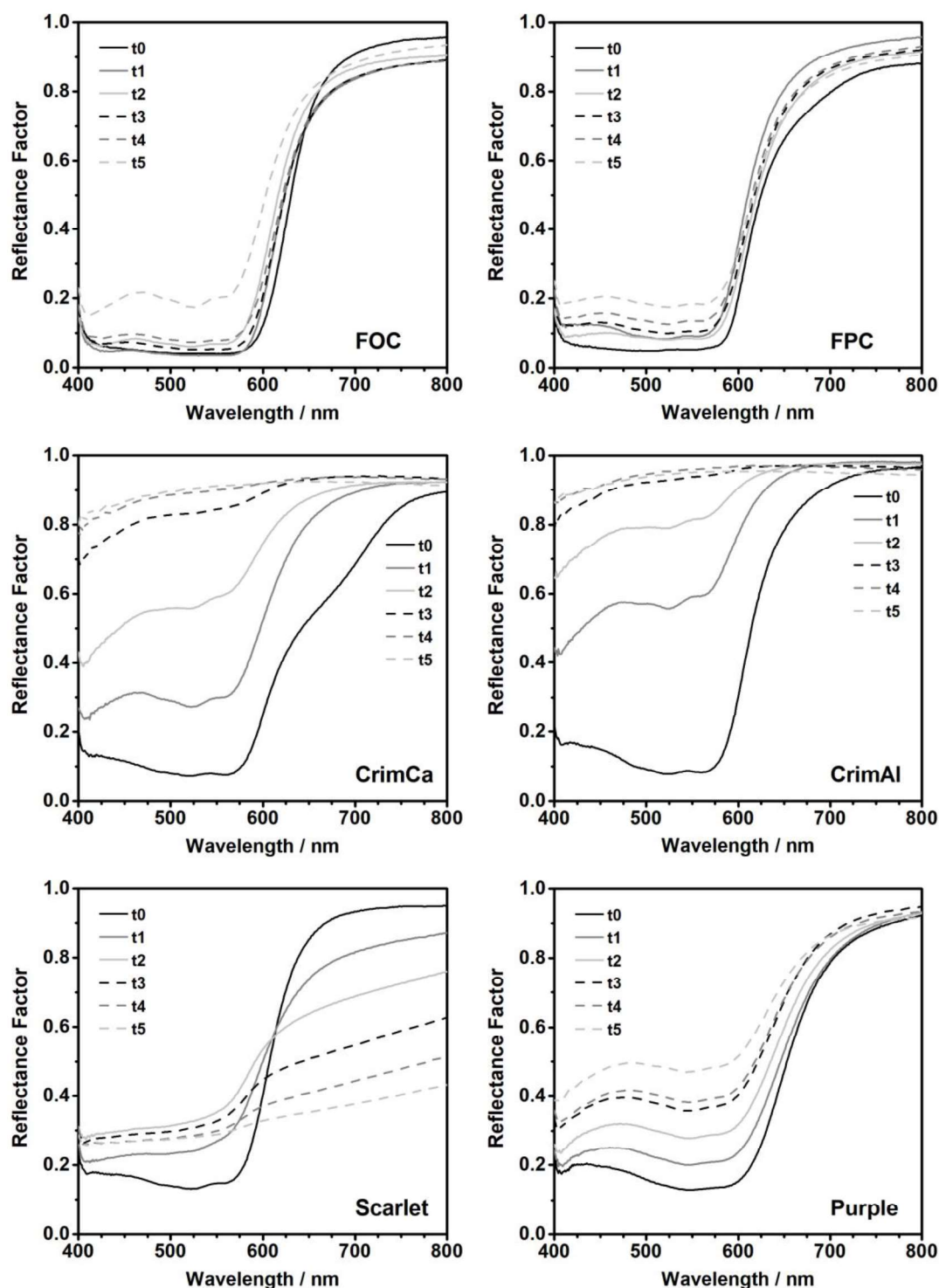


**Figure 45.** Reflectance average spectra extracted from ROIs of cochineal references with PVAc subjected to the accelerated light ageing experience.

and PVAc shows an accentuated decrease in reflectance, probably due to the characteristic blackening of vermilion (Berrie and Strumfels 2017 and references cited therein; Miliani et al. 2018).

The Purple with gum-arabic presents a strong absorption from 525 nm to 625 nm with a decrease in reflectance from t0 to t2000. On the contrary, when the Purple is mixed with PVAc, the absorbance sub-band at 547 nm is visible and the reflectance increases with the increase in the irradiation time. The Purple W&N with gum-arabic shows two sub-bands around 535 nm and 570 nm and an overall decrease in reflectance.

To identify and map on the image reconstructed from the data cube the regions with the same and distinct spectral features, starting from the work of Fu et al. 2007, an algorithm was developed by Andrea Casini using a spectroscopic approach based on the calculation of the first derivative of the spectra. In this method, PCA was first applied to the hyperspectral cube to reduce the number of components from 400 to 15 principal components that will retain the most important information of the complex dataset. The first derivative is calculated from the 15 components, as well as the zero and the maximum and minimum of the first derivative, through the statistic regression of the absorption band under the assumption that the band is similar to a gaussian function. It then determines the absorption maxima at each pixel through a parabolic fit made to the maximum and minimum of the first derivative (which correspond to the inflection points of the absorption bands). It results in a spectral profile that indicates the wavelength of the maximum of the absorption bands and sub-bands of each pixel in the image and their intensities. By attributing

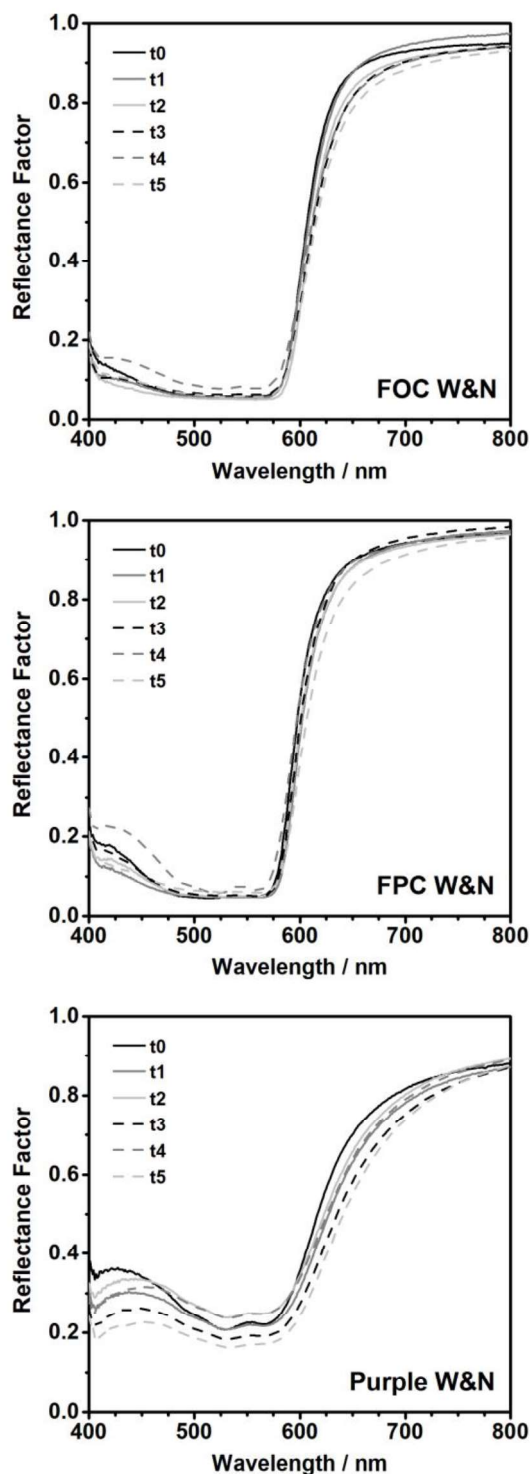


**Figure 46.** Reflectance average spectra extracted from ROIs of cochineal historical samples with gum-arabic subjected to the accelerated light ageing experience.

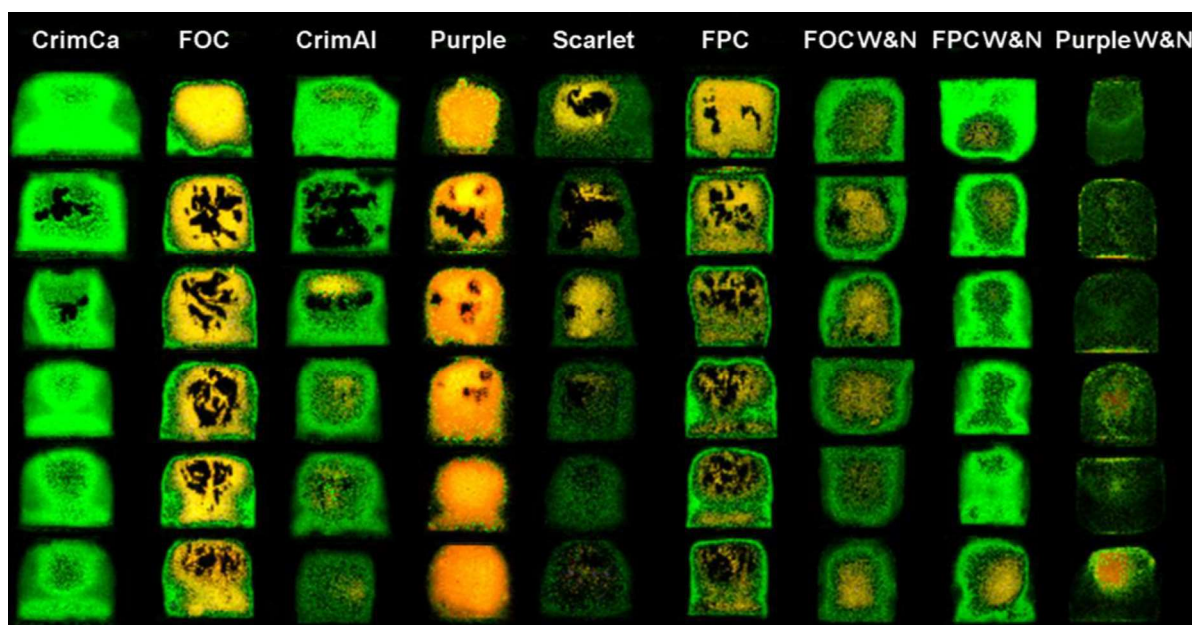


**Figure 47.** sRGB image (R 560 nm, G 522 nm, B 460 nm) with curves adjusted of gum-arabic paints subjected to the accelerated light ageing experience (from top to bottom: t 0, t 100h, t 250h, t 500h, t 1000h, t 2000h).

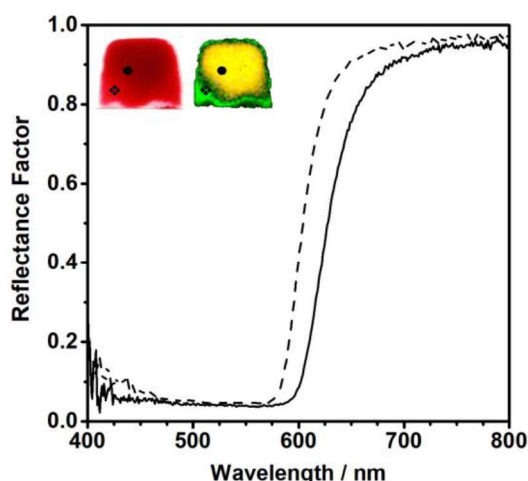


**Figure 48.** Reflectance spectra extracted from FOC with gum-arabic at t0: solid line extracted from the area marked with ● and dashed line extracted from the area marked with ♦. Inset: RGB image of the paint and respective reconstructed RGB image.

the wavelengths 460 nm, 522 nm and 560 nm to the blue, green and red channel, respectively, the reconstructed RGB image in **Figure 47** is obtained.<sup>43</sup> In this figure, all coloured pixels correspond to a combination of these three wavelengths, according to their spectral profile. Different colours in the figure therefore indicate different spectral profiles, see **Figure 48**, allowing to detect spectral variations that correspond to colour differences which may not be visible by the eye. This approach allowed to discriminate between the carmines, the crimsons, the Scarlet and the Purple painted with gum-arabic. It clearly indicates the similarity in reflectance spectral behaviour between FOC and FPC, and between CrimCa and CrimAl, as

well as the distinct characteristics of Scarlet and Purple. Not only that, it unequivocally distinguishes between the Purple reconstruction and the Purple W&N historical sample (which difference had already been evidenced through infrared spectroscopy, see Subchapter 3.2.3, pp.46,47). **Figure 47** also evidences the constant spectral behaviour throughout t0 to t2000 of those paints with gum-

<sup>43</sup> The reconstructed RGB image of the PVAc paints subjected to the accelerated light ageing experience is not shown due to the almost complete loss of colour observed.

arabic that showed the smallest colour change (e.g. CrimCa) and the difference in the spectral behaviour from t0 to t2000 of the Scarlet paint, which showed the highest colour change.

## Chapter 5

### Conclusions and Further Work

The collection of unique records in the Winsor & Newton 19th Century Archive made it possible to study and reconstruct their 19th century manufacturing processes for cochineal lake pigments. Four hundred and forty-three (443) production records pertaining to Carmine (28%), Crimson Lake (30%), Scarlet Lake (22%) and Purple Lake (20%) cochineal products were investigated. To the best of the author's knowledge, it was the first time that such study was carried, which illustrated that W&N aimed to obtain high quality, durable and reliable cochineal lakes, which pigments proved to be an important part of Winsor & Newton's production. Not only that, by reconstructing the most representative manufacturing processes for these pigments, a more complete understanding of W&N's methods of synthesis and materials used was gained.

This investigation showed that Winsor & Newton used two main processes for carmine manufacture, one headed *Finest Orient Carmine*, which involved an acid extraction of the dye and the addition of calcium ions, and the other headed *Fine Printing Carmine*, involving an alkaline extraction. The reconstruction of *Finest Orient Carmine* resulted in a finely powdered and very beautiful red pigment with a very distinctive spectral characteristic. Investigation into the alkaline extraction led to the valuable conclusion that Winsor & Newton was also adding calcium ions possibly in the form of an impure cream of tartar which allowed to obtain the same very beautiful red pigment obtained with the acid extraction. For all it is known, it was demonstrated for the first time that aluminium and calcium are both needed to obtain a carmine pigment and that aluminium alone does not produce the same result. However, it would be important to find a sample of 19th century cream of tartar to confirm that it could have been the source of calcium ions in Winsor & Newton's alkaline extraction method, as well as to investigate the influence of different quantities of calcium on the final pigments obtained. The study of W&N's crimson and scarlet processes revealed that

these pigments were produced with the addition of a dispersion of Fine Printing Carmine to an aluminate (with the further addition of vermilion for the scarlet). Winsor & Newton experimented more with their crimson processes by the addition of gypsum to replace the aluminate. The purple lake pigment was made, generally, with supernatant solutions that had already been used for the carmine, crimson and scarlet lake pigments. Most of the purple lake pigments are characterised by the addition of sulphate of zinc together with alum.

The reconstructions of 19th century cochineal lake pigments prepared following W&N's manufacturing processes for producing their carmine, crimson, scarlet and purple lakes were characterised with the complementary techniques nonextractive, nonhydrolysis SERS,  $\mu$ Raman,  $\mu$ FTIR,  $\mu$ EDXRF, ICP-AES, FORS and  $\mu$ spectrofluorimetry. To the best of the author's knowledge, this was the first time that such complementary multi-analytical approach was used to investigate the chemical composition and molecular structure of 19th century cochineal references. Comparison of the reconstructions with historical samples showed good correlation, validating the selection of the manufacturing processes most likely in use and the accuracy of the reconstructions. Five chromophores were detected, each presenting an elemental and molecular fingerprint that can be further characterised by the presence of an amorphous substrate (aluminate), an extender (gypsum), or the inorganic pigment vermilion (HgS), which are characteristic of W&N's manufacturing processes for cochineal products. Experimental evidence suggests that the presence of aluminium and calcium in the molecular structure is essential to obtain organized complexes which correspond to bright carmine pigments, while the absence of calcium probably results in a mixture of isomers of smaller complexes and purplish hues. To corroborate these hypotheses and support the definition of the molecular structures, prediction of spectra through DFT methods, as well as  $^{13}\text{C}$  and  $^{27}\text{Al}$  solid state nuclear magnetic resonance spectroscopy should be carried out.

The accelerated light ageing experience carried out with a solarbox on the reconstructions and historical samples demonstrated a greater stability of the gum-arabic paints and the overall higher lightfastness of carmines when compared with the crimson, scarlet and purple lakes. The scarlet paints showed a characteristic darkening probably explained by the blackening of vermilion. When mixed with PVAc, simulating the action of oil, the lightfastness of the paints turned out to be very poor, including an almost complete loss of colour for crimsons possibly due to the higher amount of extender.

Two additional analytical techniques were applied to study the samples subjected to the accelerated light ageing experience, microfading spectrometry and reflectance hyperspectral imaging. Microfading spectrometry is a relatively modern technique of in situ accelerated light ageing used to support lighting management in cultural heritage institutions since it helps to assess the sensitivity of colorants to light exposure. A comparison of the microfading data with those obtained with the accelerated light ageing solarbox revealed differences within results. While both methods are related with the effects of light on materials, it is important to note that microfading spectrometry is applied to measure the relative stability of colorants to light and to classify them in relation to BW standards, whereas the solarbox ageing aims to study the mechanisms of photodegradation that may occur upon irradiation and the physical consequences thereof. Bearing in mind the purpose of

microfading spectrometry and assuming that the reciprocity law is followed, this method revealed a great potentiality. It is easy to be applied and offers the advantage of being in situ and relatively fast, causing minimal and imperceptible damage to the artwork. However, the small size of the test area was proven to be a drawback regarding the representativeness of data, particularly in the case of inhomogeneous surfaces. It is advised to make several tests in different areas of the same sample to assure the accuracy of results. The importance of using adequate light sources was also shown, since different spectral power distributions may cause different colour changes. On the other hand, reflectance hyperspectral imaging proved to be an extremely powerful and valuable tool for the study of artists' materials. The enormous amount of processing that can be done with the data and the range of possibilities regarding the extraction of information is a huge advantage. In this case reflectance hyperspectral imaging allowed to analyse the reflectance behaviour of the cochineal samples in a way that the point analysis did not allow.

To conclude, an important breakthrough together with a significant set of reference materials and reference spectral data of cochineal lake pigments based on a relevant primary source has been developed and made available. It can now be used for further photodegradation studies and to investigate the chemical changes associated with; to support the development of analytical methodologies useful for the identification of these materials in artworks; and to help in the interpretation of analytical results and visual observation of paints made with these pigments.



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# Appendices



## Appendix 1. W&N's production records for cochineal products

**Table 23.** Production records for carmine.

| Name of Record                      | URC        | Date       | Manufacturing Process |
|-------------------------------------|------------|------------|-----------------------|
| Carmine                             | X6P349L01  | Jan 1855   | FOC                   |
| Carmine                             | X8P173L01  | May 1860   | FOC                   |
| Fine O. Carm. Small Batch           | X8P172L01  | Jan 1860   | FOC                   |
| Fine Orient Carmine                 | X8P149L10  | April 1858 | FOC                   |
| Fine Orient Carmine                 | X8P166L01  | April 1858 | FOC                   |
| Fine Orient Carmine                 | X8P171L01  | Dec 1859   | FOC                   |
| Fine Orient Carmine                 | X8P161L01  | June 1858  | FOC                   |
| Fine Orient Carmine                 | X8P162L01  | June 1858  | FOC                   |
| Fine Orient Carmine                 | X8P168L01  | March 1860 | FOC                   |
| Finest Orient Carmine               | P2P205AL01 | April 1858 | FOC                   |
| Finest Orient Carmine               | P3P037AL01 | April 1859 | FOC                   |
| Finest Orient Carmine               | 4PP066AL01 | April 1872 | FOC                   |
| Finest Orient Carmine               | 4PP068AL01 | April 1872 | FOC                   |
| Finest Orient Carmine               | A6P040BL01 | April 1872 | FOC                   |
| Finest Orient Carmine               | P2P307AL01 | Aug 1861   | FOC                   |
| Finest Orient Carmine               | P2P340AL01 | Aug 1863   | FOC                   |
| Finest Orient Carmine               | P2P266AL01 | Dec 1859   | FOC                   |
| Finest Orient Carmine               | P3P026AL01 | Dec 1867   | FOC                   |
| Finest Orient Carmine*              | P3P093AL01 | Feb 1870   | FOC                   |
| Finest Orient Carmine               | P2P267AL01 | Jan 1860   | FOC                   |
| Finest Orient Carmine               | P1P303BL01 | June 1858  | FOC                   |
| Finest Orient Carmine               | P2P384AL01 | March 1865 | FOC                   |
| Finest Orient Carmine               | P3P096AL01 | March 1870 | FOC                   |
| Finest Orient Carmine               | P3P097AL01 | March 1870 | FOC                   |
| Finest Orient Carmine               | 4PP051AL01 | March 1872 | FOC                   |
| Finest Orient Carmine               | P2P269AL01 | May 1860   | FOC                   |
| Finest Orient Carmine               | P3P062AL01 | May 1869   | FOC                   |
| Finest Orient Carmine               | P2P265AL01 | Nov 1859   | FOC                   |
| Finest Orient Carmine               | P3P023AL01 | Nov 1867   | FOC                   |
| Finest Orient Carmine               | P2P277AL01 | Oct 1860   | FOC                   |
| Finest Orient Carmine               | P2P219AL01 | Sept 1858  | FOC                   |
| Finest Orient Carmine               | P2P219AL01 | Sept 1858  | FOC                   |
| Finest Orient Carmine <sup>#</sup>  | P2P221AL01 | Sept 1858  | FOC                   |
| Finest Orient Carmine               | P2P276AL01 | Sept 1860  | FOC                   |
| Finest Orient Carmine <sup>\$</sup> | 4PP110AL01 | Sept 1872  | FOC                   |
| Finest Orient Carmine               | P1P212AL05 |            | FOC                   |
| Finest Orient Carmine               | X5P011AL01 |            | FOC                   |

\* This record includes two production records.

# This record includes three production records.

\$ This record includes twelve production records.

**Table 23 (cont.).** Production records for carmine.

| <b>Name of Record</b>       | <b>URC</b> | <b>Date</b> | <b>Manufacturing Process</b> |
|-----------------------------|------------|-------------|------------------------------|
| Half Orient Carmine         | X5P035AL01 |             | FOC                          |
| Orient Carmine              | X6P360L01  | Aug 1855    | FOC                          |
| Orient Carmine              | X7P001L01  | Jan 1855    | FOC                          |
| Orient Carmine              | X6P359L01  | July 1855   | FOC                          |
| Orient Carmine              | X6P351L01  | June 1855   | FOC                          |
| Orient Carmine              | X6P353L01  | June 1855   | FOC                          |
| Orient Carmine              | X6P355L01  | June 1855   | FOC                          |
| Orient Carmine              | X6P356L01  | June 1855   | FOC                          |
| Orient Carmine              | X6P358L01  | June 1855   | FOC                          |
| Orient Carmine              | X6P363L01  | Oct 1855    | FOC                          |
| Orient Carmine. The Finest  | P1P303AL01 |             | FOC                          |
| Carmine                     | 4PP109AL01 | Aug 1872    | FPC                          |
| Carmine                     | 4PP024AL01 | Feb 1871    | FPC                          |
| Carmine                     | 4PP109AL01 | Oct 1871    | FPC                          |
| Carmine                     | X5P013AL01 |             | FPC                          |
| Carmine (Old N° 2)          | P2P328AL01 | April 1863  | FPC                          |
| Carmine Paste               | X5P037AL01 |             | FPC                          |
| Carnation (Bright Lake)     | P3P084AL01 | Nov 1869    | FPC                          |
| Carnation Damp              | A6P074AL01 | Nov 1869    | FPC                          |
| Carnation Paste             | 4PP065AL01 | April 1872  | FPC                          |
| Carnation Paste*            | 4PP001AL01 | Jan 1871    | FPC                          |
| Carnation Paste             | P3P043AL01 | July 1868   | FPC                          |
| Carnation Paste*            | 4PP065AL01 | July 1872   | FPC                          |
| Damp Carmine                | P2P320AL01 | Nov 1861    | FPC                          |
| Dark Printing Carmine       | P3P027AL01 | Dec 1867    | FPC                          |
| Extra Ruby Carmine          | 4PP114AL01 | April 1873  | FPC                          |
| Extra Ruby Carmine*         | 4PP115AL01 | July 1873   | FPC                          |
| Fine Printing Carmine       | A6P060AL01 | June 1880   | FPC                          |
| Fine Printing Carmine       | A6P062AL01 | June 1880   | FPC                          |
| Finest Carnation            | A6P001BL01 | Aug 1879    | FPC                          |
| Lake Precip (Printers Carm) | X8P163L07  | July 1858   | FPC                          |
| Lake Precipitate            | 4PP073AL01 | May 1872    | FPC                          |
| Printing Carm (Rose Carm)   | P2P214AL01 | April 1858  | FPC                          |
| Printing Carm 2nd Quality   | P3P086AL01 | Dec 1869    | FPC                          |
| Printing Carmine            | P2P387AL01 | May 1865    | FPC                          |
| Printing Carmine            | P2P243AL01 |             | FPC                          |
| Printing Carmine            | X5P056AL01 |             | FPC                          |
| Ruby Carmine                | 4PP033AL01 | Aug 1871    | FPC                          |
| Ruby Carmine <sup>#</sup>   | 4PP034AL01 | Aug 1871    | FPC                          |
| Ruby Carmine                | 4PP108AL01 | Aug 1872    | FPC                          |

\* This record includes two production records.

# This record includes five production records.

**Table 23 (cont.).** Production records for carmine.

| <b>Name of Record</b>       | <b>URC</b> | <b>Date</b> | <b>Manufacturing Process</b> |
|-----------------------------|------------|-------------|------------------------------|
| Ruby Carmine*               | 4PP002AL01 | Feb 1871    | FPC                          |
| Ruby Carmine                | P3P085AL01 | Nov 1869    | FPC                          |
| Ruby Carmine                | P3P112AL01 | Nov 1870    | FPC                          |
| Ruby Carmine                | P3P080AL01 | Oct 1869    | FPC                          |
| Ruby Carmine                | P1P317AL01 |             | FPC                          |
| Ruby Carmine                | X5P014AL01 |             | FPC                          |
| Ruby Carmine                | X5P014AL01 |             | FPC                          |
| Carm. 2nd Quality O. Shade  | X6P364L01  | Feb 1856    | HOC                          |
| Carmine Half Orient         | P2P200AL01 | May 1858    | HOC                          |
| Carmine Half Orient         | P2P040AL01 |             | HOC                          |
| Carmine The Half O. Quality | P1P165AL01 |             | HOC                          |
| Carmine The Half O. Quality | P1P250AL01 |             | HOC                          |
| Carmine The Half O. Quality | P1P250AL01 |             | HOC                          |
| Carmine The Half O. Quality | P1P250AL01 |             | HOC                          |
| Carmine The Half O. Quality | P1P250AL01 |             | HOC                          |
| French Carmine              | A6P024BL01 | April 1880  | HOC                          |
| French Carmine              | A6P024BL01 | April 1880  | HOC                          |
| French Carmine              | A6P024BL01 | April 1880  | HOC                          |
| French Carmine              | A6P024BL01 | March 1880  | HOC                          |
| Half Orient Carmine         | X6P368L01  | April 1856  | HOC                          |
| Half Orient Carmine         | X6P365L01  | March 1856  | HOC                          |
| Half Orient Carmine         | X6P365L01  | March 1856  | HOC                          |
| Half Orient Carmine         | X6P366L01  | March 1856  | HOC                          |
| Half Orient Carmine         | X6P367L01  | March 1856  | HOC                          |
| Half Orient Carmine         | X6P367L01  | March 1856  | HOC                          |
| Half Orient Carmine         | X8P148L04  |             | HOC                          |
| Half Orient Carmine         | X8P151L14  |             | HOC                          |

\* This record includes two production records.

**Table 24.** Production records for crimson.

| Name of Record             | URC        | Date       | Manufacturing Process     |
|----------------------------|------------|------------|---------------------------|
| Crimson Lake               | 7PP011L01  | Jan 1842   | Crimson with Ash          |
| Crimson Lake               | 4PP158AL01 | Oct 1839   | Crimson with Ash          |
| Crimson Lake 102           | 7PP020L01  | July 1843  | Crimson with Ash          |
| Crimson Lake 107           | 7PP039L01  |            | Crimson with Ash          |
| Crimson Lake LM            | 7PP009L01  | Dec 1842   | Crimson with Ash          |
| Crimson Lake LM 135        | 7PP167L01  |            | Crimson with Ash          |
| Crimson Lake LM 135        | 9PP161L11  |            | Crimson with Ash          |
| Crimson Lake LM 145        | 7PP199L01  | June 1847  | Crimson with Ash          |
| Crimson Lake LM 145        | 9PP140L13  |            | Crimson with Ash          |
| Extra N°1 Crimson Lake     | 7PP197L01  | June 1847  | Crimson with Ash          |
| Extra N°1 Crimson Lake     | 9PP141L01  | June 1847  | Crimson with Ash          |
| Extra N°1 Crimson Lake     | 7PP145L01  | March 1846 | Crimson with Ash          |
| Extra N°1 Crimson Lake     | 7PP090L01  | May 1845   | Crimson with Ash          |
| Extra N°1 Crimson Lake     | 7PP001L02  | Oct 1843   | Crimson with Ash          |
| Extra N°1 Crimson Lake 124 | 7PP139L01  | Jan 1845   | Crimson with Ash          |
| Extra S Fine Crimson Lake  | 7PP155L01  |            | Crimson with Ash          |
| Common Crimson Lake        | 7PP138L01  | Dec 1845   | Crimson with Ash & Starch |
| Crimson Lake               | 7PP015L01  | July 1843  | Crimson with Ash & Starch |
| Crimson Lake               | 7PP195L01  | May 1847   | Crimson with Ash & Starch |
| Crimson Lake               | 9PP143L08  | May 1847   | Crimson with Ash & Starch |
| Crimson Lake 108           | 7PP049L01  | Sept 1844  | Crimson with Ash & Starch |
| Crimson Lake LM 103        | 7PP021L01  | July 1843  | Crimson with Ash & Starch |
| Crimson Lake LM 104        | 7PP022L01  | Jan 1844   | Crimson with Ash & Starch |
| Extra LM Crimson Lake 125  | 7PP140L01  | Jan 1846   | Crimson with Ash & Starch |
| Extra LM Crimson Lake 130  | 7PP149L01  | April 1846 | Crimson with Ash & Starch |
| LM Crimson Lake 109        | 7PP056L01  |            | Crimson with Ash & Starch |
| LM Crimson Lake 113        | 7PP100L01  | June 1845  | Crimson with Ash & Starch |
| LM Crimson Lake 114        | 7PP103L01  | June 1845  | Crimson with Ash & Starch |
| LM Crimson Lake 123        | 7PP137L01  | Dec 1845   | Crimson with Ash & Starch |
| LM Crimson Lake 129        | 7PP148L01  |            | Crimson with Ash & Starch |
| CM Crimson Lake            | X5P070AL01 |            | Crimson with Soda         |
| Crimson Lake LM 149        | 7PP212L01  | Aug 1847   | Crimson with Soda         |
| Crimson Lake LM 149        | 9PP132L20  | Aug 1847   | Crimson with Soda         |
| Crimson Lake LM 152        | 7PP234L01  | Oct 1847   | Crimson with Soda         |
| Crimson Lake LM 152        | 9PP119L14  | Oct 1847   | Crimson with Soda         |
| Crimson Lake LM 164        | 9PP087L01  | July 1850  | Crimson with Soda         |
| Crimson Lake LM 164        | X7P138L01  | July 1850  | Crimson with Soda         |
| Extra N° 1 Crimson Lake    | 9PP074L01  | Oct 1850   | Crimson with Soda         |
| Extra N° 1 Crimson Lake    | X7P147L01  | Oct 1850   | Crimson with Soda         |
| Extra N° 1 Crimson Lake    | 9PP019L01  | Oct 1851   | Crimson with Soda         |
| Extra N° 1 Crimson Lake    | X7P028L01  | Oct 1851   | Crimson with Soda         |

**Table 24 (cont.).** Production records for crimson.

| <b>Name of Record</b>       | <b>URC</b> | <b>Date</b> | <b>Manufacturing Process</b> |
|-----------------------------|------------|-------------|------------------------------|
| Extra N° 1 Crimson Lake     | 7PP218L01  | Sept 1847   | Crimson with Soda            |
| Extra N° 1 Crimson Lake     | 9PP129L06  | Sept 1847   | Crimson with Soda            |
| Extra Strong Crimson Lake   | 9PP007L01  | April 1853  | Crimson with Soda            |
| Extra Strong Crimson Lake   | X7P029L01  | April 1853  | Crimson with Soda            |
| Extra Strong Crimson Lake   | 9PP002L01  | Feb 1854    | Crimson with Soda            |
| Extra Strong Crimson Lake   | X7P159L01  | Feb 1854    | Crimson with Soda            |
| Extra Strong Crimson Lake   | X6P117L01  |             | Crimson with Soda            |
| Fine Crimson Lake 153       | 7PP293L01  |             | Crimson with Soda            |
| Fine Crimson Lake 153       | 9PP062L01  |             | Crimson with Soda            |
| Crimson Lake LM 147         | 7PP202L01  |             | Crimson with Soda & Starch   |
| Crimson Lake LM 147         | 9PP139L20  |             | Crimson with Soda & Starch   |
| Crimson Lake LM             | X8P152L01  |             | CrimAl                       |
| Crimson Lake LM 173         | 9PP067L01  | Jan 1851    | CrimAl                       |
| Crimson Lake LM 173         | X7P152L01  | Jan 1851    | CrimAl                       |
| Crimson Lake LM 174         | X7P156L01  |             | CrimAl                       |
| Damp Crimson Lake           | 4PP105AL01 | Aug 1872    | CrimAl                       |
| Damp Crimson Lake           | P3P116AL01 | Dec 1870    | CrimAl                       |
| Damp Crimson Lake           | 4PP005AL01 | Feb 1871    | CrimAl                       |
| Damp Crimson Lake           | A6P006AL01 | Oct 1879    | CrimAl                       |
| Damp Crimson Lake           | X5P029AL01 |             | CrimAl                       |
| Ex. Ex. Ex. Fine Crim. Lake | X5P079AL01 |             | CrimAl                       |
| Ex. Ex. Fine Crim. Lake     | X5P054AL01 |             | CrimAl                       |
| Ex. Ex. LM Crimson Lake     | X5P104AL01 |             | CrimAl                       |
| Extra Ex Fine Crimson Lake  | P3P105AL01 | Aug 1870    | CrimAl                       |
| Extra Extra Fine Crim. Lake | 4PP043AL01 |             | CrimAl                       |
| Extra Fine Crimson Lake     | P2P345AL01 | April 1866  | CrimAl                       |
| Extra Fine Crimson Lake     | 4PP046AL01 | Feb 1872    | CrimAl                       |
| Extra Fine Crimson Lake     | P2P345AL01 | Nov 1863    | CrimAl                       |
| Extra Fine Crimson Lake     | X5P051AL01 |             | CrimAl                       |
| Extra LM Crimson Lake       | X6P466L01  | July 1855   | CrimAl                       |
| Extra LM Crimson Lake       | X6P465L01  | June 1855   | CrimAl                       |
| Extra LM Crimson Lake       | P2P419AL01 | March 1866  | CrimAl                       |
| Extra LM Crimson Lake       | P1P253AL01 | Sept 1862   | CrimAl                       |
| Extra LM Crimson Lake       | P1P253AL01 |             | CrimAl                       |
| Extra LM Crimson Lake       | X5P105AL01 |             | CrimAl                       |
| Extra LM Crimson Lake 178   | 9PP025L01  |             | CrimAl                       |
| Extra N° 1 Crimson Lake     | 7PP257L01  | Feb 1848    | CrimAl                       |
| Extra N° 1 Crimson Lake     | 9PP107L01  | Feb 1848    | CrimAl                       |
| Extra N° 1 Crimson Lake     | X7P117L01  | Feb 1849    | CrimAl                       |
| Extra N° 1 Crimson Lake     | X7P130L01  | Feb 1850    | CrimAl                       |

**Table 24 (cont.).** Production records for crimson.

| <b>Name of Record</b>       | <b>URC</b> | <b>Date</b> | <b>Manufacturing Process</b> |
|-----------------------------|------------|-------------|------------------------------|
| Extra N° 1 Crimson Lake     | 7PP179L01  | Jan 1847    | CrimAl                       |
| Extra N° 1 Crimson Lake     | 9PP154L01  |             | CrimAl                       |
| Extra S Fine Crimson Lake   | 9PP184L18  |             | CrimAl                       |
| Fine Crimson Lake           | P3P107AL01 | Aug 1870    | CrimAl                       |
| Fine Crimson Lake           | 7PP253L01  | Dec 1847    | CrimAl                       |
| Fine Crimson Lake           | 9PP108L13  | Dec 1847    | CrimAl                       |
| Fine Crimson Lake           | X5P005AL01 |             | CrimAl                       |
| Fine Crimson Lake 137       | 7PP173L01  | Dec 1846    | CrimAl                       |
| Fine Crimson Lake 137       | 9PP156L15  |             | CrimAl                       |
| LM Crimon Lake              | X6P469L01  | April 1856  | CrimAl                       |
| LM Crimon Lake              | X6P469L16  | April 1856  | CrimAl                       |
| LM Crimon Lake              | P1P135AL16 |             | CrimAl                       |
| LM Crimson Lake             | X6P462L01  | Feb 1855    | CrimAl                       |
| LM Crimson Lake             | P2P391AL01 | Feb 1865    | CrimAl                       |
| LM Crimson Lake             | P2P338AL01 | July 1863   | CrimAl                       |
| LM Crimson Lake             | X6P461L01  | March 1855  | CrimAl                       |
| LM Crimson Lake             | X6P467L01  | Nov 1855    | CrimAl                       |
| LM Crimson Lake             | P3P082AL01 | Nov 1869    | CrimAl                       |
| LM Crimson Lake             | P1P366AL01 | Oct 1861    | CrimAl                       |
| LM Crimson Lake             | P2P402AL01 | Oct 1865    | CrimAl                       |
| LM Crimson Lake             | X6P123L20  | Sept 1854   | CrimAl                       |
| LM Crimson Lake             | P1P135AL16 |             | CrimAl                       |
| LM Crimson Lake             | P1P254AL01 |             | CrimAl                       |
| LM Crimson Lake             | P1P366AL01 |             | CrimAl                       |
| LM Crimson Lake             | P3P082AL01 |             | CrimAl                       |
| LM Crimson Lake             | X5P048AL01 |             | CrimAl                       |
| LM Crimson Lake             | X6P460L01  |             | CrimAl                       |
| LM Crimson Lake Ex. Quality | X6P468L01  | March 1856  | CrimAl                       |
| MM Crimson Lake             | 4PP045AL01 | Feb 1872    | CrimAl                       |
| MM Crimson Lake             | 4PP019AL01 | May 1871    | CrimAl                       |
| MM Crimson Lake             | X5P050AL01 |             | CrimAl                       |
| NM Crimson Lake             | 4PP032AL01 | Aug 1871    | CrimAl                       |
| NM Crimson Lake             | X5P053AL01 |             | CrimAl                       |
| Soft Crimson Lake LM 176    | 9PP026L15  |             | CrimAl                       |
| Soft Crimson Lake LM 176    | X7P027L01  |             | CrimAl                       |
| X Fine Crimson Lake         | P3P088AL01 | Jan 1870    | CrimAl                       |
| XXLM Crimson Lake           | P3P079AL01 | Sept 1869   | CrimAl                       |
| Crimson Lake for Oil        | A5P045AL01 | Dec 1879    | CrimCa                       |
| Crimson Lake for Oil        | A5P062AL01 | June 1878   | CrimCa                       |
| Crimson Lake for Oil        | P3P031AL01 | March 1868  | CrimCa                       |
| Crimson Lake for Oil        | P3P110AL01 | Sept 1870   | CrimCa                       |

**Table 24 (cont.).** Production records for crimson.

| <b>Name of Record</b>                    | <b>URC</b> | <b>Date</b> | <b>Manufacturing Process</b> |
|------------------------------------------|------------|-------------|------------------------------|
| Crimson Lake for Oil                     | X5P045AL01 |             | CrimCa                       |
| Crimson Lake for Oil Grin.               | X6P474L01  | Sept 1855   | CrimCa                       |
| Rough Cr. Lake for Oil Grin.             | X6P459L01  | April 1856  | CrimCa                       |
| Rough Cr. Lake for Oil Grin.             | X6P457L01  | Feb 1856    | CrimCa                       |
| Rough Cr. Lake for Oil Grin.             | X6P475L01  |             | CrimCa                       |
| Rough Crimson                            | X7P030L01  | March 1855  | CrimCa                       |
| Rough Crimson Lake                       | P2P257AL06 | May 1866    | CrimCa                       |
| Rough Crimson Lake                       | P2P257AL06 | Nov 1859    | CrimCa                       |
| Rough Crimson Lake for Oil               | P1P110AL06 |             | CrimCa                       |
| Rough Crimson Lake for Oil               | P1P110AL06 |             | CrimCa                       |
| Crimson Lake <sup>#</sup>                | 7PP193L01  | May 1847    |                              |
| Crimson Lake <sup>#</sup>                | 9PP144L01  | May 1847    |                              |
| Crimson Lake LM 167 <sup>#</sup>         | 9PP081L01  |             |                              |
| Crimson Rose <sup>#</sup>                | P1P111AL01 |             |                              |
| Drop Lake LM 141 <sup>#</sup>            | 7PP188L01  | May 1847    |                              |
| Drop Lake LM 141 <sup>#</sup>            | 9PP148L01  | May 1847    |                              |
| Drop Lake LM 150 <sup>#</sup>            | 7PP215L01  | Aug 1847    |                              |
| Drop Lake LM 150 <sup>#</sup>            | 9PP131L01  | Aug 1847    |                              |
| Extra Extra Crimson Lake <sup>#</sup>    | P1P185AL01 |             |                              |
| Extra Extra Crimson Lake <sup>#</sup>    | P1P185AL01 |             |                              |
| Extra Extra Crimson Lake <sup>#</sup>    | X8P153L01  |             |                              |
| Extra Extra Fine Crim. Lake <sup>#</sup> | X6P478L01  | April 1855  |                              |
| Extra Extra Fine Crim. Lake <sup>#</sup> | P2P367AL01 | July 1864   |                              |
| Extra Extra Fine Crim. Lake <sup>#</sup> | P2P321AL01 | Nov 1861    |                              |
| Extra Fine Crimson Lake <sup>#</sup>     | X6P471L01  | July 1855   |                              |
| Extra Fine Crimson Lake <sup>#</sup>     | 9PP008L01  | March 1853  |                              |
| Extra Fine Crimson Lake <sup>#</sup>     | X6P477L01  | March 1855  |                              |
| Extra Fine Crimson Lake <sup>#</sup>     | X7P023L01  | May 1850    |                              |
| Extra M Crimson Lake <sup>#</sup>        | X6P464L01  | May 1855    |                              |
| Extra N° 1 Crimson Lake <sup>#</sup>     | X7P119L01  | April 1849  |                              |
| Extra N° 1 Crimson Lake <sup>#</sup>     | X7P021L01  | April 1850  |                              |
| Extra N° 1 Crimson Lake <sup>#</sup>     | X7P157L01  | June 1851   |                              |
| Extra N° 1 Crimson Lake <sup>#</sup>     | 9PP024L01  | June 1851   |                              |
| Extra N° 1 Crimson Lake <sup>#</sup>     | X7P017L01  | May 1849    |                              |
| Extra Strong Crimson Lake <sup>#</sup>   | X7P164L01  | June 1855   |                              |
| Fine Crimson Lake <sup>#</sup>           | P2P361AL01 | April 1864  |                              |
| Fine Crimson Lake <sup>#</sup>           | P2P166AL01 | March 1859  |                              |
| Fine Crimson Lake <sup>#</sup>           | X6P119L01  | Oct 1853    |                              |
| Fine Crimson Lake <sup>#</sup>           | P1P237BL01 |             |                              |
| Fine Crimson Lake 148 <sup>#</sup>       | 7PP205L01  | May 1847    |                              |

<sup>#</sup> Records with no corresponding manufacturing process and/or which are not clear and consequently are not included in the final count.

**Table 24 (cont.).** Production records for crimson.

| Name of Record                          | URC       | Date       | Manufacturing Process |
|-----------------------------------------|-----------|------------|-----------------------|
| Fine Crimson Lake 175 <sup>#</sup>      | 9PP137L12 | Aug 1847   |                       |
| Fine Crimson Lake 175 <sup>#</sup>      | X7P025L01 | March 1851 |                       |
| Fine Crimson Lake 175 <sup>#</sup>      | 9PP027L01 | March 1851 |                       |
| LM Crimson Lake <sup>#</sup>            | X6P463L01 | May 1855   |                       |
| LM Crimson Lake <sup>#</sup>            | X6P122L19 | Nov 1853   |                       |
| LM Crimson Lake <sup>#</sup>            | X6P121L01 | Oct 1853   |                       |
| LM Crimson Lake <sup>#</sup>            | X6P122L01 | Oct 1853   |                       |
| LM Crimson Lake 110 <sup>#</sup>        | 7PP057L01 | Nov 1844   |                       |
| LM Crimson Lake 115 <sup>#</sup>        | 7PP106L01 | July 1845  |                       |
| LM Crimson Lake 131 <sup>#</sup>        | 7PP153L01 | June 1845  |                       |
| LM Crimson Lake 131 <sup>#</sup>        | 9PP186L04 | June 1845  |                       |
| LM Crimson Lake 132 <sup>#</sup>        | 7PP157L01 |            |                       |
| LM Crimson Lake 132 <sup>#</sup>        | 9PP183L16 |            |                       |
| LM Crimson Lake 144 <sup>#</sup>        | 7PP196L01 |            |                       |
| LM Crimson Lake 144 <sup>#</sup>        | 9PP142L13 |            |                       |
| LM Crimson Lake 146 <sup>#</sup>        | 7PP200L01 |            |                       |
| LM Crimson Lake 154 <sup>#</sup>        | 7PP309L01 | Aug 1848   |                       |
| LM Crimson Lake 154 <sup>#</sup>        | 9PP053L01 | Aug 1848   |                       |
| LM Crimson Lake 155 <sup>#</sup>        | 7PP317L01 | Aug 1848   |                       |
| LM Crimson Lake 155 <sup>#</sup>        | 9PP049L01 | Aug 1848   |                       |
| LM Crimson Lake 161 <sup>#</sup>        | X7P114L01 | Jan 1849   |                       |
| LM Crimson Lake 162 <sup>#</sup>        | X7P128L01 | Dec 1849   |                       |
| LM Crimson Lake 162 <sup>#</sup>        | X7P019L01 |            |                       |
| LM Crimson Lake 167 <sup>#</sup>        | X7P141L01 | Aug 1850   |                       |
| LM Crimson Lake 181 <sup>#</sup>        | 9PP024L01 |            |                       |
| Rough Crimson Lake for Oil <sup>#</sup> | X7P031L01 | March 1855 |                       |
| T Crimson Lake for Tubes <sup>#</sup>   | 7PP089L01 | May 1845   |                       |

<sup>#</sup> Records with no corresponding manufacturing process and/or which are not clear and consequently are not included in the final count.

**Table 25.** Production records for scarlet.

| <b>Name of Record</b>           | <b>URC</b> | <b>Date</b> | <b>Manufacturing Process</b> |
|---------------------------------|------------|-------------|------------------------------|
| Scarlet Lake                    | 7PP014L01  | Feb 1843    | Scarlet with Ash             |
| Scarlet Lake N° 1               | 7PP010L01  | Jan 1843    | Scarlet with Ash             |
| Scarlet Lake N° 127             | 7PP144L01  | Feb 1846    | Scarlet with Ash             |
| Scarlet Lake N° 128             | 7PP147L01  |             | Scarlet with Ash             |
| Scarlet Lake 105                | 7PP028L01  | Feb 1844    | Scarlet with Ash & Starch    |
| Scarlet Lake LM 134             | 7PP161L01  |             | Scarlet with Ash & Starch    |
| Scarlet Lake LM 134             | 9PP165L01  |             | Scarlet with Ash & Starch    |
| Scarlet Lake S 100              | 7PP017L01  | July 1843   | Scarlet with Ash & Starch    |
| Scarlet Lake S 101              | 7PP019L01  | July 1843   | Scarlet with Ash & Starch    |
| T Scarlet Lake for Tubes        | 7PP096L01  | June 1844   | Scarlet with Ash & Starch    |
| Tube Scarlet Lake 133           | 7PP160L01  | June 1844   | Scarlet with Ash & Starch    |
| Tube Scarlet Lake 133           | 9PP181L07  | June 1844   | Scarlet with Ash & Starch    |
| Damp Scarlet Lake               | 4PP004AL01 | Feb 1871    | Scarlet                      |
| Damp Scarlet Lake               | P2P382AL01 | Jan 1865    | Scarlet                      |
| Damp Scarlet Lake               | P3P001AL01 | Jan 1867    | Scarlet                      |
| Damp Scarlet Lake               | P2P390AL01 | June 1865   | Scarlet                      |
| Damp Scarlet Lake               | 4PP004AL01 | Nov 1871    | Scarlet                      |
| Damp Scarlet Lake               | P2P441AL01 | Oct 1866    | Scarlet                      |
| Damp Scarlet Lake               | P2P274AL01 | Sept 1860   | Scarlet                      |
| Damp Scarlet Lake               | A5P006AL01 |             | Scarlet                      |
| Ex Ex Fine Scarlet Lake         | A5P070AL01 | June 1879   | Scarlet                      |
| Ex Ex Fine Scarlet Lake         | 4PP006AL01 | March 1871  | Scarlet                      |
| Ex Ex Fine Scarlet Lake         | X5P076L01  |             | Scarlet                      |
| Extra Fine Scarlet Lake (trial) | P1P180BL11 |             | Scarlet                      |
| Extra LM Scarlet Lake           | X5P058L01  |             | Scarlet                      |
| Fine Scarlet Damp Lake          | X6P480L01  | Feb 1856    | Scarlet                      |
| Fine Scarlet Damp Lake          | P1P354AL01 |             | Scarlet                      |
| Fine Scarlet Lake               | P1P242AL01 | April 1858  | Scarlet                      |
| Fine Scarlet Lake               | X8P159L01  | April 1858  | Scarlet                      |
| Fine Scarlet Lake               | P1P242AL01 |             | Scarlet                      |
| Fine Scarlet Lake               | X5P009L01  |             | Scarlet                      |
| Fine Scarlet Lake 140           | 7PP183L01  | March 1847  | Scarlet                      |
| Fine Scarlet Lake 140           | 9PP151L01  | March 1847  | Scarlet                      |
| LM Scarlet Lake                 | P3P094AL01 | Feb 1870    | Scarlet                      |
| LM Scarlet Lake                 | P2P356AL01 | Jan 1864    | Scarlet                      |
| LM Scarlet Lake                 | X5P080L01  |             | Scarlet                      |
| Marbler's Scarlet Lake          | P2P241AL01 | March 1859  | Scarlet                      |
| Marbler's Scarlet Lake          | P2P334AL01 | March 1863  | Scarlet                      |
| Marbler's Scarlet Lake          | P1P371AL01 |             | Scarlet                      |
| Marbler's Scarlet Lake          | P1P371AL01 |             | Scarlet                      |
| MM Scarlet Lake                 | P3P099AL01 | March 1870  | Scarlet                      |

**Table 25 (cont.).** Production records for scarlet.

| Name of Record              | URC        | Date       | Manufacturing Process          |
|-----------------------------|------------|------------|--------------------------------|
| MM Scarlet Lake             | X5P069L01  |            | Scarlet                        |
| N M Scarlet Lake            | 4PP028AL01 | July 1871  | Scarlet                        |
| NM Scarlet Lake             | X5P068L01  |            | Scarlet                        |
| N°2 Marbler's Scarlet Lake  | P3P056AL01 | Mar 1869   | Scarlet                        |
| Scarlet Damp Lake           | P2P227AL01 | Oct 1858   | Scarlet                        |
| Scarlet Lake LM 136         | 7PP170L01  |            | Scarlet                        |
| Scarlet Lake LM 136         | 9PP159L09  |            | Scarlet                        |
| Scarlet Lake LM 137         | 7PP171L01  |            | Scarlet                        |
| Scarlet Lake LM 137         | 9PP158L13  |            | Scarlet                        |
| Scarlet Lake LM 139         | 7PP180L01  |            | Scarlet                        |
| Scarlet Lake LM 139         | 9PP153L08  |            | Scarlet                        |
| Ex Fine Scarlet Lake N° 188 | 9PP005L01  | May 1853   | Scarlet with Amm. Carb. & Soda |
| Ex Fine Scarlet Lake N° 188 | X7P042L01  | May 1853   | Scarlet with Amm. Carb. & Soda |
| Fine Scarlet Lake           | 9PP018L01  | June 1852  | Scarlet with Amm. Carb. & Soda |
| Fine Scarlet Lake           | X7P040L01  | June 1852  | Scarlet with Amm. Carb. & Soda |
| Fine Scarlet Lake           | P1P130AL01 |            | Scarlet with Amm. Carb. & Soda |
| Fine Scarlet Lake           | X6P484L01  |            | Scarlet with Amm. Carb. & Soda |
| Fine Scarlet Lake           | X6P485L20  |            | Scarlet with Amm. Carb. & Soda |
| Fine Scarlet Lake N° 177    | X7P038L01  | April 1851 | Scarlet with Amm. Carb. & Soda |
| Damp Scarlet Lake           | 4PP071AL01 | Jan 1873   | Scarlet with Soda              |
| Damp Scarlet Lake           | 4PP049AL01 | March 1872 | Scarlet with Soda              |
| Damp Scarlet Lake           | 4PP071AL01 | March 1873 | Scarlet with Soda              |
| Damp Scarlet Lake           | 4PP071AL01 | May 1872   | Scarlet with Soda              |
| Damp Scarlet Lake           | X5P004AL01 |            | Scarlet with Soda              |
| Ex Marbler's Scrlt Lake 163 | 9PP088L01  | June 1850  | Scarlet with Soda              |
| Ex Marbler's Scrlt Lake 163 | X7P137L01  | June 1850  | Scarlet with Soda              |
| Ex Marbler's Scrlt Lake 168 | 9PP077L01  | June 1850  | Scarlet with Soda              |
| Ex Marbler's Scrlt Lake 168 | X7P145L01  | June 1850  | Scarlet with Soda              |
| Fine LM Scarlet Lake N° 190 | X7P044L01  | Aug 1854   | Scarlet with Soda              |
| Fine Scarlet Lake           | X6P120L01  | Aug 1854   | Scarlet with Soda              |
| Fine Scarlet Lake           | X6P483L01  | July 1855  | Scarlet with Soda              |
| Fine Scarlet Lake           | X6P484L13  | Sept 1855  | Scarlet with Soda              |
| Fine Scarlet Lake N° 160    | X7P112L01  | Jan 1849   | Scarlet with Soda              |
| Fine Scarlet Lake 140       | P1P092AL04 | March 1847 | Scarlet with Soda              |
| Fine Scarlet Lake 151       | 7PP229L01  |            | Scarlet with Soda              |

**Table 25 (cont.).** Production records for scarlet.

| <b>Name of Record</b>                       | <b>URC</b> | <b>Date</b> | <b>Manufacturing Process</b> |
|---------------------------------------------|------------|-------------|------------------------------|
| Fine Scarlet Lake 157                       | 7PP336L01  | Sept 1848   | Scarlet with Soda            |
| Fine Scarlet Lake 157                       | 9PP038L01  | Sept 1848   | Scarlet with Soda            |
| Fine Scarlet Lake 157                       | P1P087AL04 | Sept 1848   | Scarlet with Soda            |
| Fine Scarlet Lake 157                       | 9PP124L01  |             | Scarlet with Soda            |
| Fine Scarlet Lake N° 177                    | 9PP025L01  | April 1851  | Scarlet with Soda            |
| Lake for Marbler's                          | P1P087AL01 |             | Scarlet with Soda            |
| LM Carriage Lake                            | X5P099AL01 |             | Scarlet with Soda            |
| LM Scarlet Lake                             | X6P132L01  | July 1854   | Scarlet with Soda            |
| LM Scarlet Lake 158                         | P1P086AL18 | Sept 1848   | Scarlet with Soda            |
| Marbler's Scarlet Lake 163                  | X7P112L01  | May 1850    | Scarlet with Soda            |
| MM Carriage Lake                            | A6P070AL04 | Jan 1877    | Scarlet with Soda            |
| MM Carriage Lake                            | A6P069BL01 | June 1880   | Scarlet with Soda            |
| MM Scarlet Lake                             | A5P020AL18 | Sept 1879   | Scarlet with Soda            |
| Scarlet Lake LM 156                         | 7PP331L01  |             | Scarlet with Soda            |
| Scarlet Lake LM 156                         | 9PP041L01  |             | Scarlet with Soda            |
| Scarlet Lake LM 158                         | 7PP338L01  | Sept 1848   | Scarlet with Soda            |
| Scarlet Lake LM 158                         | 9PP037L01  | Sept 1848   | Scarlet with Soda            |
| Scarlet Lake N° 159                         | 7PP342L01  | Jan 1848    | Scarlet with Soda            |
| ScrIt Lake (Marbler's) N° 159               | 9PP035L01  | Jan 1848    | Scarlet with Soda            |
| ScrIt Lake (Marbler's) N° 159               | P1P086AL01 | Jan 1848    | Scarlet with Soda            |
| Damp Scarlet Lake <sup>#</sup>              | P2P390AL01 | April 1866  |                              |
| Experiments for Scarlet Lake <sup>#</sup>   | P1P086BL02 |             |                              |
| Extra Fine Scarlet Lake <sup>#</sup>        | 4PP074AL01 | May 1872    |                              |
| Extra Fine Scarlet Lake <sup>#</sup>        | X5P046AL01 |             |                              |
| Extra Fine Scarlet Lake <sup>#</sup>        | P1P180AL14 |             |                              |
| Fine Scarlet Lake <sup>#</sup>              | X8P170L01  | Dec 1859    |                              |
| Fine Scarlet Lake <sup>#</sup>              | P2P413AL01 | Fev 1866    |                              |
| Fine Scarlet Lake <sup>#</sup>              | P2P316AL01 | Jan 1863    |                              |
| Fine Scarlet Lake <sup>#</sup>              | P2P316AL01 | Oct 1861    |                              |
| Fine Scarlet Lake 142 <sup>#</sup>          | 7PP190L01  |             |                              |
| Fine Scarlet Lake 142 <sup>#</sup>          | 9PP145L01  |             |                              |
| Marbler's Scarlet Lake <sup>#</sup>         | P3P022AL01 | Nov 1867    |                              |
| Marbler's Scarlet Lake <sup>#</sup>         | A6P033BL01 |             |                              |
| Scarlet Lake Xpt <sup>#</sup>               | X8P124L01  | Dec 1854    |                              |
| Scarlet Lake Xpt <sup>#</sup>               | X8P125L09  | Mar 1855    |                              |
| Small Trial Mrblr's ScrIt Lake <sup>#</sup> | X6P486L01  |             |                              |

<sup>#</sup> Records with no corresponding manufacturing process and/or which are not clear and consequently are not included in the final count.

**Table 26.** Production records for purple.

| Name of Record                                           | URC        | Date       |
|----------------------------------------------------------|------------|------------|
| Best Deep Purple Lake                                    | P1P369AL03 |            |
| Best Deep Purple Lake                                    | P2P294AL01 | Jan 1862   |
| Best Deep Purple Lake                                    | X6P116L01  | Aug 1854   |
| Best Deep Purple Lake                                    | X6P452L01  | June 1855  |
| Best Light Purple Lake                                   | P3P066AL01 | April 1869 |
| Best Light Purple Lake                                   | P3P091AL01 | March 1870 |
| Best Light Purple Lake                                   | PMP216L01  |            |
| Black Purple Lake                                        | P2P333AL01 | Feb 1863   |
| Blue Purple No.2                                         | 7PP012L01  | Jan 1842   |
| Blue Purple No.2                                         | 7PP013L01  | Jan 1842   |
| Blue Purple No.2                                         | X2P011L01  | Jan 1842   |
| Blue Purple No.2                                         | X2P012L01  | Jan 1842   |
| Coachers Deep Purple Lake No 55                          | 7PP156L01  | July 1846  |
| Coachers Purple Lake (Deep) No. 55                       | X2P134L01  | July 1836  |
| Coachmakers Deep Purple Lake No 55                       | 9PP184L01  | July 1846  |
| Cochineal Purple. (1739)                                 | P2P261AL01 | Sept 1859  |
| Damp Purple Lake                                         | P2P261AL17 |            |
| Dark Purple (No. 51)                                     | 7PP068L01  | Sept 1844  |
| Dark Purple (No. 51)                                     | X2P057L01  |            |
| Deep Purple Colour from Supernatant of Cochineal boiling | 7PP248L01  | Dec 1847   |
| Deep Purple Colour from Supernatant of Cochineal boiling | X2P212L01  | Dec 1847   |
| Deep Purple Lake                                         | P4P042L01  | Nov 1837   |
| Deep Purple Lake                                         | X6P114L01  | Sept 1853  |
| Deep Purple Lake                                         | X6P114L25  | Nov 1853   |
| Deep Purple Lake                                         | X6P453L01  | Nov 1855   |
| Deep Purple Lake                                         | X7P134L01  | March 1850 |
| Deep Purple Lake (1759)                                  | P1P209AL11 |            |
| Deep Purple Lake (54)                                    | 7PP143L01  | Feb 1846   |
| Deep Purple Lake 54                                      | X2P123L01  | Feb 1846   |
| Deep Purple Lake No 56                                   | 7PP158L01  | Aug 1846   |
| Deep Purple Lake No 56                                   | 9PP182L06  | Aug 1846   |
| Deep Purple Lake No. 70                                  | 9PP176L01  | Nov 1852   |
| Deep Purple Lake. Fine Quality                           | P2P278AL01 | Sept 1858  |
| Extra Deep Purple Lake                                   | P2P186AL01 |            |
| Extra Deep Purple Lake                                   | P3P120AL01 | May 1871   |
| Extra Deep Purple Lake                                   | X5P066AL01 |            |
| Extra Deep Purple Lake 57                                | 7PP172L01  | Dec 1846   |
| Extra Deep Purple Lake 57                                | 9PP157L16  | Dec 1846   |
| Extra Deep Purple Lake 57                                | X2P148L01  | Dec 1846   |
| Extra Extra Deep Purple Lake                             | P3P108AL01 | Aug 1870   |
| Extra Extra Deep Purple Lake                             | PMP220L01  |            |
| Extra Extra Deep Purple Lake for Water                   | X5P081AL01 |            |

**Table 26 (cont.).** Production records for purple.

| <b>Name of Record</b>                               | <b>URC</b> | <b>Date</b> |
|-----------------------------------------------------|------------|-------------|
| Indian Purple                                       | 4PP047AL01 | Feb 1872    |
| Indian Purple                                       | 9PP007L01  | March 1853  |
| Indian Purple                                       | A5P065AL01 | Feb 1872    |
| Indian Purple                                       | P1P256AL01 |             |
| Indian Purple                                       | P2P395AL01 | Out 1864    |
| Indian Purple                                       | X5P049AL01 |             |
| Indian Purple                                       | X7P089L01  | Sept 1856   |
| Intense or Black Purple Lake                        | 7PP150L01  |             |
| Intense or Black Purple Lake                        | X2P129L01  |             |
| Light Purple Lake (No 62)                           | 7PP319L01  |             |
| Light Purple Lake (No 62)                           | 9PP048L01  |             |
| Light Purple Lake from Waste Liquors                | 7PP303L01  | Aug 1848    |
| Light Purple Lake from Waste Liquors                | 9PP057L01  | Aug 1848    |
| Light Purple Lake from Waste Liquors                | X2P252L01  | Aug 1848    |
| No. 36 Deep Purple Lake                             | X2P136L01  | Aug 1846    |
| No. 50 Purple Lake                                  | 7PP051L01  | Sept 1844   |
| No. 50 Purple Lake                                  | X2P045L01  | Sept 1844   |
| No. 60 Purple Lake                                  | X2P254L01  | Aug 1848    |
| No. 62 Light Purple Lake                            | X2P265L01  |             |
| No. 64 Light Purple Lake to match LB's              | X7P015L01  | March 1849  |
| No. 65 Deep Purple Lake                             | X7P013L01  | Aug 1849    |
| Purple                                              | 3PP098L01  | Jan 1838    |
| Purple                                              | 3PP152L01  | Mar 1838    |
| Purple Colour from Supernatant of Cochineal boiling | 9PP111L01  | Dec 1847    |
| Purple Lake                                         | 3PP037L01  |             |
| Purple Lake                                         | 3PP056L01  | Dec 1839    |
| Purple Lake                                         | A6P004AL13 |             |
| Purple Lake                                         | P1P284AL06 |             |
| Purple Lake                                         | PMP218L01  |             |
| Purple Lake                                         | PMP236L01  |             |
| Purple Lake – best light                            | P2P234AL01 | Jan 1858    |
| Purple Lake (No 60)                                 | 7PP307L01  | Aug 1848    |
| Purple Lake (No 60)                                 | 9PP055L01  | Aug 1848    |
| Purple Lake (No 63) L B's Tint                      | 7PP334L01  | Sept 1848   |
| Purple Lake (No 63) L B's Tint                      | 9PP038L01  | Sept 1848   |
| Purple Lake Best Crimson Shade                      | X5P039AL01 |             |
| Purple Lake Direct from the Cochineal               | 7PP163L01  | Sept 1846   |
| Purple Lake Direct from the Cochineal               | 9PP163L07  | Sept 1846   |
| Purple Lake Direct from the Cochineal               | X2P141L01  | Sept 1846   |
| Purple Lake Experiment                              | 7PP047L01  | Sept 1844   |
| Purple Lake from Grouts                             | 3PP308L01  | Mar 1839    |
| Purple Lake in Oil (Artists')                       | P2P084AL01 |             |

**Table 26 (cont.).** Production records for purple.

| <b>Name of Record</b>   | <b>URC</b> | <b>Date</b> |
|-------------------------|------------|-------------|
| Purple Lake No. 63      | X2P276L01  | Sept 1848   |
| Rough Purple Lake       | P1P355AL01 |             |
| Strong Deep Purple Lake | 7PP240L01  | Nov 1847    |
| Strong Deep Purple Lake | 9PP116L01  | Nov 1847    |
| Strong Deep Purple Lake | X2P206L01  |             |

## Appendix 2. List of W&N abbreviations and interpreted names

**Table 27.** W&N abbreviations within cochineal records and interpreted names.

| W&N Abbreviation                | Interpreted Name                    | W&N Abbreviation                                     | Interpreted Name             |
|---------------------------------|-------------------------------------|------------------------------------------------------|------------------------------|
| Ac Ac, Acet Ac                  | Acetic Acid                         | Grout                                                | Dregs                        |
| Aq                              | Water                               | H:O:                                                 | Half Orient                  |
| Al, A                           | Alum                                | Liqr                                                 | Liquor                       |
| A, Potash, P Ash, P. A.         | Pearlash                            | N W                                                  | New Milk                     |
| A la Mon                        | Monro's Method of Cochineal Boiling | P V, P Verm                                          | Pale Vermilion               |
| Ammo                            | Ammonia                             | Prec, Precip, Pcp, PP                                | Precipitate                  |
| Bi Tartrate Potash, Bi T P, BTP | Cream Tartar                        | Plaster Paris, Superf Plaster, Superf PP             | Calcium Sulphate Hemihydrate |
| Bor Soda, B S                   | Borax                               | R Carm                                               | Rough Carmine                |
| Cit Ac, C. Ac, C A              | Citric Acid                         | Sct Lake                                             | Scarlet Lake                 |
| Carb Ammo, C A                  | Ammonium Carbonate                  | Sedts                                                | Sediments                    |
| Coch Mex Blk                    | Cochineal Mexican Black             | Soda, Sod, S, Carb Soda                              | Sodium Carbonate             |
| Cr Tart, C T                    | Cream Tartar                        | Sol                                                  | Solution                     |
| Crim Lake, Cr Lake              | Crimson lake                        | Sub C P, SCP, Sub Carb Potassa, PLN, Salts of Tartar | Potassium Carbonate          |
| DRC                             | Dissolved Rough Carmine             | Sul Zinc, Sul Z, S Z, Zinc Sulp                      | Zinc Sulphate                |
| Expt                            | Experiment                          | Supt                                                 | Supernatant                  |
| F                               | Ferment Patent Yeast                | Wt St                                                | White Starch                 |

## Appendix 3. Experimental Section

### 3.1. Materials

For the preparation of the carminic acid reference and reconstructions of Winsor & Newton cochineal lake pigments and paints the following reagents of analytical grade were used: carminic acid (229253), alum (aluminium potassium sulphate dodecahydrate,  $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ), borax (sodium tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), plaster of Paris (calcium sulphate hemihydrate,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ), vermilion (mercury(II) sulphide,  $\text{HgS}$ ), and PVAc ( $[\text{CH}_2\text{CH}(\text{O}_2\text{CCH}_3)]_n$ ) from Sigma-Aldrich; citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) and zinc sulphate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) from Panreac; cream of tartar (potassium hydrogen tartrate,  $\text{KC}_4\text{H}_5\text{O}_6$ ) from Scharlau; calcium carbonate ( $\text{CaCO}_3$ ) from Roig Farma; and ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ) from Alfa Aesar. Cochineal (36040) and gum-arabic from Kremer Pigmente, and fresh milk from Vigor were also used.

For the preparation of the colloidal silver nanoparticles used for the SERS analyses, potassium nitrate ( $\text{KNO}_3$ ) from Riedel-de Haën, silver nitrate ( $\text{AgNO}_3$ ) from Merck, and sodium citrate tribasic dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) from Sigma-Aldrich were used.

For the preparation of the samples for ICP-AES analyses, nitric acid ( $\text{HNO}_3$  69%) from Panreac was used.

Millipore water was used on all occasions.

### 3.2. Apparatus

pH measurements were carried out with a Sartorius Docu-pH Meter. Calibration was performed with pH 4 and 7 buffer solutions from Panreac.

X-ray fluorescence data was obtained with an ArtTAX spectrometer, Intax GmbH, with a molybdenum (Mo) anode, Xflash detector refrigerated by the Peltier effect (Sidrift) and a mobile arm. The spatial resolution was 70 mm and the following experimental parameters were used: 35 kV of voltage, 300  $\mu\text{A}$  of intensity, and 300 seconds of acquisition time.

The ICP-AES analyses were performed at the REQUIMTE Analysis Laboratory (NOVA University of Lisbon). The determination of the elements Al, Ca, B and Zn was carried out in a ICP (Inductively Coupled Plasma-Atomic Emission Spectrometer) Horiba Jobin-Yvon, France, Ultima, model equipped with a 40.68 MHz RF generator, Czerny-Turner monochromator with 1,00 m (sequential) and autosampler AS500. Samples were analysed in aqueous solution. Circa 3 mg of sample were digested with  $\text{HNO}_3$  69% in an ultrasonic bath at ca. 70 °C. After complete dissolution, the  $\text{HNO}_3$  solution was diluted with water to a total volume of 2 mL and 10% concentration (v/v) and put again in the ultrasonic bath. Analyses were only carried out in one sample for each reference due to the high amount of sample required.

SERS and Raman spectra were collected with a Horiba Jobin-Yvon Labram 300 spectrometer equipped with a HeNe laser of 17mW power operating at 632.8 nm. Spectra were recorded as an extended scan. The laser beam was focused with an Olympus 50x objective lens. The laser power at the sample was controlled with the use of a neutral density filter with 0.3 optical density (8.5 mW). All samples were analysed with a laser exposure time of 15 seconds for 15 scans.

Infrared analyses were carried out using a Nicolet Nexus spectrophotometer coupled to a Continuum microscope (15× objective) with a MCT-A detector cooled by liquid nitrogen. Spectra were obtained in transmission mode, between 4000 and 650  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$  and 128 or 256 scans. Samples were previously compressed using a Thermo diamond anvil compression cell. Spectra are shown here as acquired, without corrections or any further manipulations, except for the occasional removal of the  $\text{CO}_2$  absorption at ca. 2300-2400  $\text{cm}^{-1}$ .

Fluorescence excitation and emission spectra were recorded on a Jovin-Yvon SPEX Fluorog 3-2.2 spectrofluorometer coupled to an Olympus BX51 M confocal microscope, with spatial resolution controlled with a multiple-pinhole turret, corresponding to a minimum 2  $\mu\text{m}$  and maximum 60  $\mu\text{m}$  spot, with a 50× objective. Standard dichroic filters of 525 and 570 nm were used at 45° to collect the emission and excitation spectra, respectively. Emission spectra were acquired by exciting at 510-515 nm and excitation spectra were carried out collecting the signal at 590-600 nm. Both were acquired in a 30  $\mu\text{m}$  spot (pinhole 8) and the following slits set: emission slits = 3/3/3 mm, and excitation slits = 5/3/0.8 mm. The optimisation of the signal, through mirror alignment in the optic pathway of the microscope, was performed. Spectra were collected after focusing on the sample (eye view) followed by signal intensity optimisation (detector reading). Emission and excitation spectra were acquired in the same spot whenever possible.

FORS measurements were performed using two Zeiss spectroanalysers equipped with optical fibres: a MCS 601 UV/VIS model (with a 1024 Si photodiode array sensor) operating in the 190-1025 nm range, and a MCS 611 NIR 2.2 WR model (with a 256 InGaAs photodiode array detector) operating in the 910-2200 nm range, with a resolution of approximately 0.8 and 5.0 nm/pixel, respectively. A tungsten-halogen lamp (Zeiss model CLH600) was used. The 0°/2x45° reflectance configuration was adopted to avoid specular reflectance. A 99% Spectralon diffuse reflectance standard was used for calibration.

For measuring colour, a portable spectrophotometer colourimetry Data Color International was used. Its measuring head's optical system uses diffuse illumination from a pulsed Xenon arc lamp over the 8 mm-diameter measuring area, with 0° viewing angle geometry. The calibration was performed with a white bright standard plate and a total black standard.

The absorption spectra in solution were recorded with a UV-Vis-NIR Cary Varian 5000 spectrophotometer and absorbances were corrected to dilution.

Emission spectra were obtained using a Spex Fluorolog 212 I Horiba spectrofluorimeter upon excitation at 420 nm.

### 3.3 Experimental Section

The colloidal silver nanoparticles used for the SERS analyses were prepared by chemical reduction of the metal salt silver nitrate with sodium citrate following the procedure published by Lee and Meisel 1982. A 5-fold more concentrated colloid was used. The silver nanoparticles were prepared as follows: 100 mL of a  $5 \times 10^{-3}$  M silver nitrate aqueous solution were brought to gentle reflux under magnetic stirring in a two-neck round-bottom flask wrapped in aluminium foil and equipped with a thermometer and a condenser to prevent evaporation. When boiling, 2 mL of a 5% w/v aqueous solution of sodium citrate were slowly added dropwise always keeping the boiling and the vigorous magnetic stirring. The colour of the solution turned into greyish green, indicating the reduction of the  $\text{Ag}^+$  ions. The solution was kept under magnetic stirring and in reflux for approximately one hour. Heating was then discontinued, and the solution was left under magnetic stirring until it slowly cooled down to room temperature. When not in use, the colloid solution (pH 8.1) was kept in the refrigerator in the dark, and it was stable for several months with reproducible results. A 0.5 M potassium nitrate aqueous solution was also prepared and used as the aggregating agent. When not in use, the aggregant solution was kept at room temperature. The SERS spectrum of the silver colloid after the addition of the aggregant in a proportion 5:1 is presented in **Figure 49**. It exhibits signals in the  $1100\text{--}750\text{ cm}^{-1}$  and  $1500\text{--}1300\text{ cm}^{-1}$  regions related to the citrate ion and to by-products of the reduction reaction (Munro et al. 1995; Leona, Stenger, and Ferloni 2006 and reference cited therein).

For carminic acid and the Winsor & Newton cochineal lake pigment reconstructions, in which a higher quantity of sample was available, 50  $\mu\text{L}$  of the silver colloid and 10  $\mu\text{L}$  of the aggregant solution were deposited directly onto each sample in powder form in a lid of an Eppendorf. For the historical pigment samples, 30  $\mu\text{L}$  of the silver colloid and 6  $\mu\text{L}$  of the aggregant solution were used in the same way. For the paint samples from tubes of oil paint, in which a small quantity of sample was available, 10  $\mu\text{L}$  of the silver colloid and 2  $\mu\text{L}$  of the aggregant solution were deposited directly onto micro-samples of the paints in a lid of an Eppendorf. SERS spectra were collected by focusing the laser

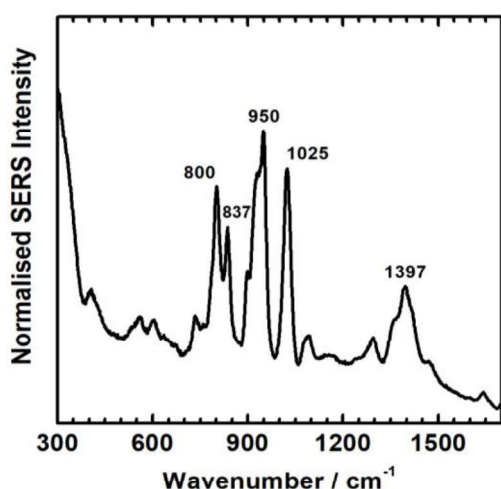


**Figure 49.** SERS spectrum of the silver colloid after the addition of the aggregant (0.5 M  $\text{KNO}_3$ ) in a proportion 5:1.

beam onto the aggregates that formed inside the analyte-colloid droplet immediately after the deposition of the silver colloid and aggregant in the lid of the Eppendorf. Several spectra were acquired continuously and the best spectra obtained were selected. More than one sample from each reference was analysed to assure reproducibility. It should also be noted that Raman was tried on the pigments with lasers 632.8 nm and 785 nm and no good signal was obtained. The Raman spectra were featureless and displayed high fluorescence background.

Carminic acid from Sigma-Aldrich and a reference of carminic acid precipitated with aluminium (designated as CA-Al) were used for supporting the interpretation of molecular data. For preparation of the CA-Al reference, colour was extracted from cochineal insects in an aqueous solution with potassium carbonate, and alum was added until precipitation of a purplish pigment at neutral pH. The precipitate was centrifugated, washed with water and allowed to air-dry.

Gum-arabic and PVAc paints were prepared by hand-grinding 0.05 g of each pigment with a pestle on an agate mortar and adding 20 drops of a 10% gum-arabic solution and 15 drops of a PVAc solution (20% (w/v) in acetone), respectively. Paints were applied onto glass slides with a Zehntner GmbH applicator ZAF 2010.6050 (50 µm). For the accelerated light ageing experience, all paints were previously applied on the glass slides with a drawdown applicator.

For the preparation of the reconstructions of Winsor & Newton cochineal lake pigments the following conversion table was used for the extrapolation of the ingredient quantities:

**Table 28.** Conversion table.

| <b>Liquid Measures</b> | <b>Abbreviations</b> | <b>Metric Equivalents (mL)</b> |
|------------------------|----------------------|--------------------------------|
| 1 dram                 | 1 dr.                | 3.55                           |
| 1 meg pot              | 1 mp.                | 47.333                         |
| 1 gill                 | 1 gill               | 142                            |
| 1 pint                 | 1 pt.                | 568                            |
| 1 quart                | 1 qt.                | 1136                           |
| 1 gallon               | 1 gal.               | 4540                           |
| <b>Weight Measures</b> | <b>Abbreviations</b> | <b>Metric Equivalents (g)</b>  |
| 1 grain                | 1 gr.                | 0.0648                         |
| 1 dram                 | 1 dr.                | 1.772                          |
| 1 ounce                | 1 oz.                | 28.35                          |
| 1 pound                | 1 lb.                | 453.6                          |
| 1 hundredweight        | 1 cwt.               | 50800                          |
| <b>Length</b>          | <b>Abbreviations</b> | <b>Metric Equivalents (cm)</b> |
| 1 inch                 | 1 in.                | 2.54                           |
| 1 foot                 | 1 ft.                | 30.48                          |
| <b>Temperature</b>     | <b>Abbreviations</b> | <b>Celsius (°C)</b>            |
| 212 Fahrenheit         | 212 °F               | 100                            |

The micro-sample of carmine paint used to validate the reconstruction of FOC as an accurate reference of an historical W&N carmine was taken from the painting *Untitled (Coty)*, Amadeo de Souza-Cardoso, c. 1917, oil on canvas, Calouste Gulbenkian Foundation, **Figure 50**, and is presented as red sample µ6 in the work of Cristina Montagner (Montagner 2015, p.97). The micro-sampling was carried out in the context of the study of the materials and techniques of Amadeo de Souza-Cardoso.

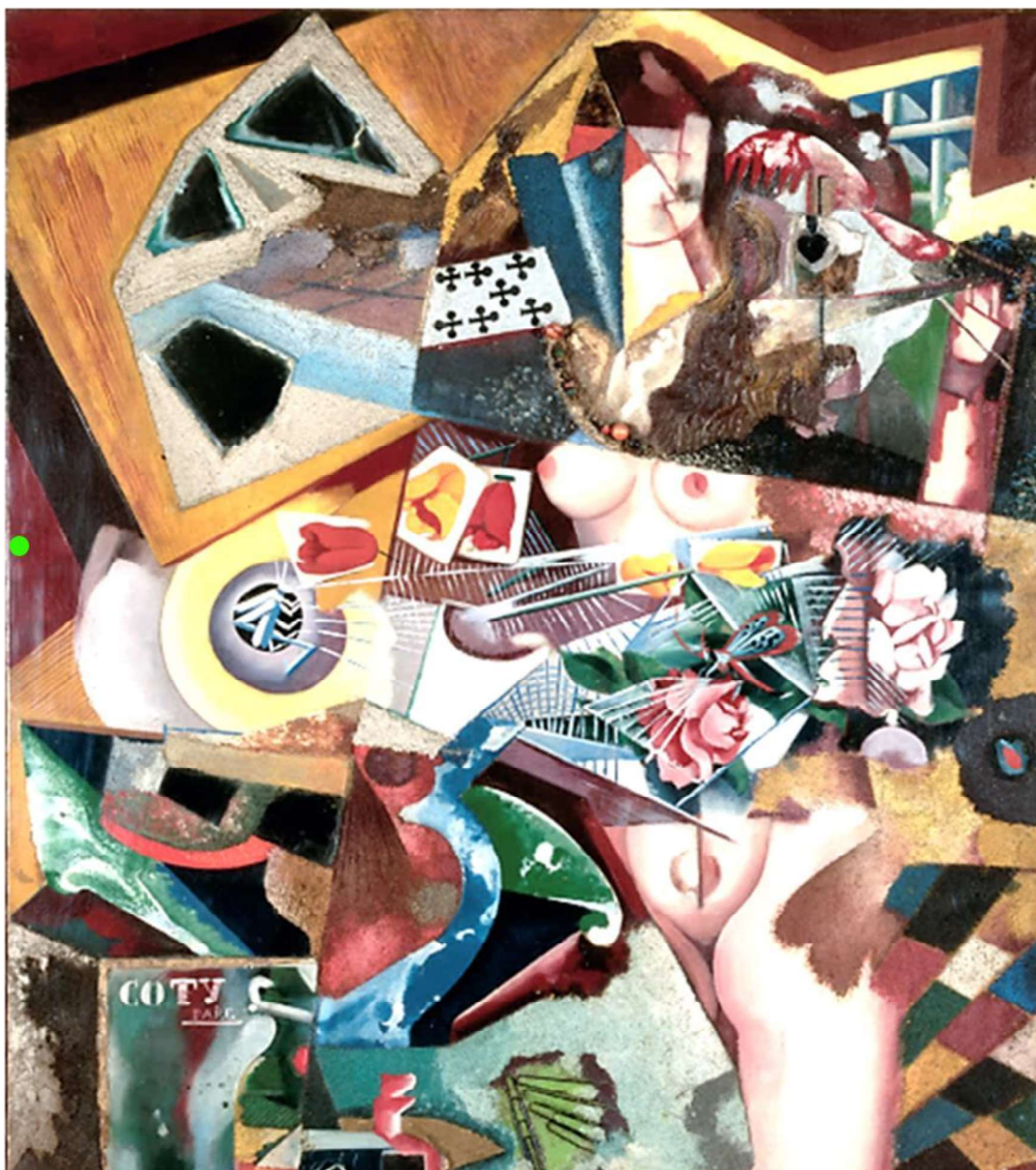


**Figure 50.** *Untitled (Coty)*, c. 1917, oil on canvas, Amadeo de Souza-Cardoso. Calouste Gulbenkian Foundation, Lisbon. The micro-sampling area is indicated with ● (see Montagner 2015, p.194). Photo by Cristina Montagner.

## Appendix 4. Transcription of Winsor & Newton 19th century cochineal recipes

### Finest Orient Carmine | URC 4PP110AL01

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Finest Orient Carmine

Q/5605. September 30. 1872

2831. Large steam-vat that had been cleaned out previously by boiling with water that had had ½ lb cit: ac: added when boiling, boil 1 hour then run away & scrub the vat out with water to thoroughly rinse

2832. To the clean empty vat [2831] add 3 ft 3 in cold clear rain aq, when 212° turn off steam, add immediately 28 lbs coch'l Mexican black [19/9/72] crushed

Add immediately 28 oz C: A: turn on steam to 212°

Boil @ 212° 15 minutes from the time the steam is turned on after addition of the CA

Turn off steam, strain

Add at 183° (i.e. immediately after straining) 9 galls N: M: [as fresh milked as possible & perfectly genuine] poured in out of the cows in a steady regular stream, so as to take 8 minutes over the operation, then leave closely covered up 1 hour

Draw off bright (from sediments) & run into clean well tinned copper, turn on steam to 210° - 212° as quickly as possible, two persons skimming surface of scum

Turn off steam sufficiently to keep the liquor @ 208° - 209° add 56 oz B: S: (powdered & sifted)

Stir well 5 minutes

Add 28 oz A: (picked lump pot: al: powdered & sifted)

Stir for 10 minutes, & regulate heat so that it is kept at 208° - 209°

During this time, at the expiration of these 10 minutes the liquor just bubbles round the edge of the copper & is 210°. Turn off steam & run out to settle

Next day draw off supernatant liquor turbid but affording hardly any tint, on paper, when tried with alkali

Strain, filter, chalk & dry off as [2673]<sup>44</sup>

Produce = 57 oz nett (oct 9 72)

Q/5606 8/10/72 Batch with 28 lbs coch'l mex: blk [1108 / 19/9/72] worked as [2831/2832]

Q/5625 5/11/72 Batch with 28 lbs coch'l mex: blk [8938 / 24/5/72] worked as [2831/2832]

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<sup>44</sup> Marginal number from URC 4PP051AL01 (Finest Orient Carmine):

"2673. Next day, draw off supernatant liquor. A little turbid, but exceedingly weak, so much so that with alkali it hardly stains white paper. Strain carefully 2ce & filter on two(?) clothes. Next day, scrape well down often. Next day, chalk on clean dry chalk stones with fine linen (not thin) placed between the ? chalk & the silk cloth which takes the color, put on top chalks as well. Done as soon after 8 am as possible same day, about 6 pm, take color off chalks, cut out & put on cleaned ? boards, carmine ones, & put in drying room (upper) & dry off at not exceeding 70°. Produce = 64 oz nett."

Q/5643 3/12/72 Batch worked same as 25/11/2 p 111

Q/5710 28/5/73 Batch as [5/5/73] but the CA ? of L. B. Lawes 10/5/73)

Q/5740 24/6/73 Batch as [28/5/73] Q/5710

Would a nice carmine be produced by boiling the same quantity of cochl with less CA, but precipitating with same quantities of B:S: & A: & using no N M?

It might produce a bright & cheaper article, & match the best French?

Would a much finer quality of "Orient" be produced by taking more cochineal to the same quantity of other ingredients?

The artificial flower makers say they want a carmine to match the "scarlet geranium"

#### Notes

Q/5606 Oct 22. '72. Batch: worked as [2831/2] in the heating & skimming, the liquor was not allowed to exceed about 210° before the BS was added

Produce = 61½ oz nett

Q/5643 Nov 25th '72. Batch: worked as [2831/2] 176° was the heat at which the NM was added, Took 9 min to pour it in, bright liquor got up to 210° when skimmed slackened heat to 206° - 208° during the 5 minutes stirring after addition of the BS. The A added at 206° - 208° then heat gradually got up to 210° & no more even at the expiration of the final 10 minutes stirring & heating, the stirring was brisk during the first 5 minutes of the 10, & slow during the remr of it

Produce = 57½ oz nett

Q/5644 Dec 16th '72. Batch: worked as [2831/2] & [Nov 25th 72 batch] but the liquor was 188° when the NM was added

Produce = 61 oz nett

#### Notes:

Q/5644 January 13 1873 Batch worked as [2831/2 & Nov 25' 72]

But the liquor was 190° when the NM was added

Produce = 63 oz nett 23/1/73

Q/5645 April 21 1873 Batch: worked as [2831/2 & Nov 25' 72]

But the liquor was 192° when the NM was added, while the liquor, in copper, was waiting for bottoms? to filter, it was kept at 180°

Produce = 59½ oz nett 30/4/73

Q/5710 May 5 1873 Batch: worked as [2831/2, Nov 25' 72 & April 21st '73] but the liquor was allowed to fall in temper to 202° by the expiration of the 5 min stirring immediately before the addition of the Al:

Produce = 59½ oz nett, 13/5/73

NB. Although the working of the batches extended over a period from sept 1872 until July 1873 with very little intermission, the only variations from the formula [Q/5605] are those named in the foregoing notes

Carmine The H:O: Quality

For No 40 French or for Oil grinding

748. Water in large copper to within 3½ inches of top as described [580]<sup>45</sup> add 20 lbs Mex cochl (black)

Add immediately 20 oz cit: acid & boil 15 min, strain & leave the liquor 2 hours as [580]

749. Treat the settled liquor as [581]<sup>45</sup> with 40 oz bor soda, 20 oz alum & boil for 20 minutes, then bale into clean butt

750. Treat as at [582 & 583]<sup>45</sup> but before drying off mix into the carmine pulp 1 gill of acetic acid stirred in with a wooden spoon

Filter for about 1 hour longer, then put the colour into the press & press it gradually & well then take it out of the linen filter & keep it in the silk one. Then place it between chalk stones with white blotting paper between the silk filter & the chalk. When as much water has absorbed as possible, then dry the carmine off in the silk filter placed on a dropping board, at a heat of about 80°

Mem: This batch was dried off without any heat at all in the drying room, the fire not having been lighted at all. When the water had been absorbed by the chalks the carmine was taken out of the silk filter & placed in small pieces on flat boards to dry. Produce 54 lbs. Dried with hardly any mouldiness, was bright & nice looking

32 oz of this parcel were sent to Whipple & Co & sold to them under the name of "French Carm: N° 40"

Notes. The carmine is to be filtered on silk filter placed over a linen one.

Cost of batch incomplete

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<sup>45</sup> Marginal number from URC P1P165AL01 (Carmine. The H:O: Quality):

"580. In a copper capable of holding 120 gallons, put cold water to within 4 inches from the top. Make the water boil. Then slacken the heat a little merely by opening the door of the furnace & shutting the door of the ashpit. Add continuously 20 oz citric acid, stir till dissolved, then add 20 lbs Mexican cochineal that had been crushed or ground in a mill. Boil for 15 minutes<sup>#</sup> then strain through sieve & put the clear liquor into a 90 gallon butt. Leave 2 hours for the sediments to subside. Then draw off carefully from the sediments. The sediments are now to be put on a filter so that as much clear liquor may be got away as possible\*.

581. Put the clear liquor back into the clean copper & boil up<sup>‡</sup>, then add 40 oz borate of soda (finely pounded) when dissolved add 20 oz alum (powdered potash sort) & continue to boil 20 minutes<sup>#</sup>, then bale into a clean butt for the carmine to settle.

582. After the carmine has thus stood 5 or 6 days & sometimes a shorter period the carmine has completely deposited & the clear supernatant liquor is found to be very poor.

583. Draw off the supernatant liquor & put the carmine on filter, then put the colour on chalk stone with fine linen placed between & afterwards dried off in square cakes on open boards in drying room.

<sup>#</sup> The carmine is the better for a very moderate heat in boiling. We have made a very successful boiling by keeping the heat from 205° to 210°.

\* The quantity of grouts left in the filter after the transparent liquor had drained away was ½ gallon.

<sup>‡</sup> When the liquor boils skim off the froth that rises to the surface."

Another way. Prepared as 748-749 & treated with ½ gill strong

A. Acet: acid ( ? & Co, South Lambeth) well stirred in, then chalk the color on linen & finally dry off at a moderate heat (80°) on open trays. This produced a very bright carmine when thoroughly dry Was not far short in color to the "Finest Orient"

This carmine has a nice yellow hue. Is fully equal to the ordinary "French Carmine" such as we could depend upon receiving from Lefranc & Co à Paris - So equal to Baker's Best Carmine or very nearly so. The acet: acid prevents the carmine from turning mouldy & effectually preserves the bright tint in drying off

There is danger of deteriorating the carmine by drying on chalk after ac ac has been used in the pulp. Any ac ac left would attack the chalk & form the salt acetate of lime. Sulphate of lime would not be touched by acet ac "HCN" "A compound block might be formed of sulphate of barytes (common sort) & plaster of Paris neither would be affected by acet acid HCN

Another way

B. Prepared as 748-749 but the heat to begin with was 195°. Boiling at the heat 15 min: gradually bringing up to 205°

Draw off clear liquor & treat at 180° with the BS & Al. gradually bringing up to 212°, only allowing it to arrive at the latter heat 5 minutes before the fire was drawn. Produce 57 oz nett when quite dry. The Carmine settled quickly. This boiling was not slimey.

Another way. Prepared as 748-749, but the heat to begin with

C. [748] was 203° increasing to 210° during 15 minutes

The clear liquor heated again to 208° & kept at a bubbling heat for 20 minutes during the forming of the carmine. This was chalked before the acet acid was added. Then put into pan & beaten well up with ½ gill of the acet: acid: then dropped off spoon on the clean paper placed in dropping boards. The Carmine dried very well this way & was not mouldy in the least. Was but a very little slimey. Less than former.

## **Fine Printing Carmine | URC A6P060AL01**

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Fine Printing Carmine

7597. June 24. 1880

32.

In 340 gallon steam-worm vat put 250 gallons cold (New River) aq. When \* 212°, turn off steam. Cool to 210°, add

36 lbs cochineal Teneriffe Black crushed. Lightly shed in & well stirred in till heat down to 206° Sprinkled in

4 lbs S:C:P: [30/6/79] exsicc: stir well 5 minutes add

1 lb 14 oz Al: (Lppp&d) stir well 3 minutes, strain, wash grouts with 12 galls boiling aq. Leave in

settling vat ¼ hour for sediments to subside. Draw off bright liquor close down to sediments

Add to bright liquor at 142° 12 oz Al: (Lppp&d) stir well 5 min add 8 lbs C:T: (pulv) [6/11/79] (extra dried in drying room) carefully shed in & well stirred & stirring continued for ¼ hour afterwards then leave till next day

Next day draw off exceedingly # weak supernatant (this supernatant with p. ash afforded the faintest possible tint of pink on paper)

Strain & filter settled colour

Thus far, the above process is same as "N° 1 Scarlet Lake Precip"

\* At a violent boil (steam in boiler being 34? To the ? inch) see p 62

# This supernatant was perfectly transparent

Tr.A. A little of the filtered pulp as other side was treated with ac: ac: chalked & dried off

Produced a bright rich tinted "Printing Carmine" in dry state & in oil

Probably an improved process & cheaper?

Tr.B. A little of the unprecipitated liquor was treated with more Al: (than the proportion of 12 oz) & precipitated with CT pulv quantities unknown. Seemed to yield a much more bulky precip: with weaker supt. The precip: was bright crimson & transparent

Same character as ? Carnation look probably brighter

## **Rough Crimson Lake | URC P1P110AL06**

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Rough Crimson Lake for oil

[439] Prepare 42 lbs of superfine plaster Paris (bought of Stevens & Son of Drury Lane) by sifting it dry through a hair sieve into a 250 gallon butt half full of cold water, another person stirring all the time, when all sifted in, continue to stir for 2 hours, be careful that none of the plaster clogs at the bottom of the butt. Next day draw off supernatant water and strain it through as fine a sieve as it will go through, if the plaster is too thick add more water to thin it, put the strained plaster into another 250 gallon butt and now leave for a fortnight\*

[440] Prepare lake precipitate from 8 x 6 lbs Mexican cochineal = 48 lbs altogether, each 6 lbs prepared as at [423]<sup>46</sup> and when filtered of its supernatant take off filter and work through sieve into

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<sup>46</sup> Marginal number from URC P1P097AL01 (Double Lake Liquor):

"423. To prepare lake liquor by the best process we have yet discovered, we take 6 lbs of Mexican cochineal ground (? of A Johnson) and boiled as follows: in a copper worm tub (the tub itself is made of thick deal) vide fig. 45 capable of holding 50 gallons put 41 galls of cold clear water which just covers the top of the worm. Now turn on the steam which passes through the worm & makes the water boil (it takes from 20 min: to ½ hour). When the water boils<sup>+</sup> add 12 oz of salts of tartar (carb: potasse P.L.N.) when dissolved & well mixed in turn off the steam this of course instantly causes the water to cease boiling but instantly add the 6 lbs cochineal & stir well in, continue stirring for 5 minutes then add 6 oz of powdered potash alum and stir & mix well for 3 minutes longer, then strain through a rather open cypress sieve so that the liquor will just run through without

sufficient cold water to make it run fluid through a (?) syphon [fig 46, page 101] into the prepared plaster of Paris [439] that had had its supernatant water drawn off close to the settled body. During the time the diluted Lake precipitate is being syphoned into the plaster body, the whole must be well stirred, after all in, take out stick and leave for the colour to settle.

Next day, draw off the supernatant liquor which is but very slightly tinted red and being of no use may run away, strain the lake and put it on filters. When filtered well press it & dry off in square cakes on clean dropping boards at a heat of about 90° to 100° # when dry the colour is powdered roughly for oil grinding. Produce 54 lbs nett.

Notes:

\* We think that by leaving the plaster under water for this period, we deprive it of a portion of its causticity thereby preventing the cochineal crimson colouring matter from becoming purpled

# By drying off at a good heat we avoid the colour drying mouldy on the surface

About Dec 1854 we made some trials on a palette between the old alumina (LM) lakes for oil and the plaster lake [439 & c.] we found that the latter was the freshest in tint, after having been exposed to the light and air till June 1857

This was sold under the name of "Rose Crimson" to Lithografns @ 12/lb was roughly powdered first.

This Crimson Lake is very transparent, rich and strong in oil and has the advantage over aluminous bodies lakes, in not getting fat in oil.

Formula 439A. Plaster body as [439] strain carefully. Draw off supernatant water off the body, add 52 galls Lake precipitate liquor (strength 1 lb coch to 1 gallon), strain, filter, prep and dry off. Produce 55 lbs nett

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beating the sieve & yet keep back the grouts and feculae. The whole of the strained liquor is put into a clean butt (empty) the grouts that remain behind have certainly a little colouring matter left in them, but of a poor character. These grouts are put by for boiling for purple lakes [ ]. When the strained liquor has cooled down to 145° \* add 1½ lbs of cream of tartar in powder, stirring all the time it is being sprinkled in & continue to stir well for 10 minutes or ¼ hour after all is in. To stir well and long at this stage of the process is an essential point for on this depends the perfect precipitation of the colour. If this process is carefully worked the colour will settle very perfectly and leave the supernatant liquor very poor & weak in colour and perfectly transparent and the settled colour bright and strong. If the colour is wanted & it has settled well it can be drawn off the next day but we think it advisable to let it stand a few days so as to make sure that all the colour has gone down.

‡ The water must boil violently & the effervescence come up to the top of the tub just avoiding coming over, then the carb pot: added, stirred in & then the steam turned off immediately before adding the cochineal.

\* Some cochineal requires a stronger heat. 150° to 155° has often been the best heat for some qualities of cochineal."

## **Crimson Lake | URC 4PP045AL01**

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M M Crimson Lake

P/5402. Feb 1872

2652. Prepare 4 x 250 gallons vats, each as under:

14 lbs CA in 20 gallons boiling aq

44 lbs A in 40 gallons boiling aq

Stir ¼ hr fill up with cold aq

Next day draw off supernatant

Wash settled body twice

Cold aq, 1ce daily

2653. Prepare lake precipitate liquor as under:

Large steam-vat 2 ft 8½ cold aq, 212°

Slacken steam to a simmer

211° Add 3 lbs S:C:P: [Howards'] stir 1 min

Add at a simmer 211° 24 lbs CochI Teneriffe black [4/10/70] crushed, stir 1 minute well

Turn on steam & boil as at [2635] for 30 minutes, turn off steam, add 1½ lb A: (Lppp) stir 3 minutes

Strain, add at 145° 6 lbs CT (powd:) [Howards'] (took 5 min to shed in) stir ¼ hr longer & leave for color to settle

2654. Another 24 lbs cochI Teneriffe blk [4/10/70] same as [2653]

2655. Draw off transparent & weak supernatant of [2653/4]

Strain settled color, filter & make into 48 galls liquor as usual

2656. To the washed & settled body [2652] syphon in the 48 galls liquor [2655]

Strain, filter, press, drop & dry off in upper

Lake room @ 70°

Produce = 58 lbs

## **Scarlet Lake | URC 4PP006AL01**

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Ex: Ex: Fine Scarlet Lake Or Finest Marblers'

P/5094. March 6 1871

2539. Large steam-vat 2 ft 8½ cold aq

When 212° add 3 lbs S:C:P: [HK & Co's very dry] stir 1 min

Turn off steam, add immediately 24 lbs CochI Mex: Blk [18/1/71] crushed,

Stir well 5 min, add slowly sprinkled in & well stirred 1½ lb Al: (Lppp) stir 3 min, strain,

Add at 155° 6 lb CT [DY & R's powd] carefully & slowly sprinkled in, then further stir ¼ hr & leave

2540. Another 24 lbs CochI same as [2539]

2541. " 24 lbs " " " "

2542. “ 24 lbs “ “ “ “

2543. “ 24 lbs “ “ “ “

2544. Draw off supernatant from settled color of [2539]

[2540 to 2543] Strain & filter settled color, when well drained, make into 120 galls liquor as usual, strain into butt, & leave for sediments to subside, when required for use, stir up 1 or 2 hrs before drawg off, this allows the sediments to subside, & the bright pure liquor is drawn off for use the sediments which are black looking, & having no good color left in them, are thrown in with the grouts

2545. Prepare body with (250 gallon empty vat)

10/3/71. 14 lbs C:A: in 20 galls boiling aq

56 lbs Al: (Lpp) in 56 galls boiling aq

Stir ¼ hr turn into empty 500 gallon “liquor” vat & leave till next day

Next day draw off supernatant from settled body (supernant? Drawn off close(?) to settled body.

Wake? said that about 20 or 30 gallons of supernatant liquor were drawn off from settled body)

2546. Wash the body 1ce only filling the

11/3/71 vat to within 18 inches of the top

Work in as usual 12x4 lbs (= 48 lbs) P: V: [24/2/71]

Syphon in the

11/3/71 120 gallons liquor [2544]

12/3/71 (Sunday)

13/3/71 draw off transparent supernatant which had a very faint tint of pink, but nothing to notice, strain settled color very carefully & put on filters, press, drop & dry off in upper lake room @ 70° or 75°

The two windows of the drying room were open day & night to cause a constant current of fresh air through the room

Produce = 89 lbs 5 Oz nett

Contain about 1½ lb cochl & ½ PV to each 1 lb lake

January 8 1872 Examined & found to be non-adhesive to the tongue, quite non-absorbent, & bright & rich in color

Skim milk introduced into the body during the making is said to stop the absorbent quality of alumina & to render it suitable for Marblers' Lakes & ? The milk also prevents it from grinding frothy

Told so by M. Monro. July 1872

I have little doubt of it ?

Because M. Stark(?) of Glasgow has so often laid stress on the solid “painty” character of a good “Marblers” Lake

By the above means, a variety of colors might be prepared for Marblers

M. Monro said that there must be no grease remaining in the milk.

Best Deep Purple Lake

992. Take 6 boilings of grouts of cochineal boilings [748]<sup>47</sup> or [889]<sup>48</sup> each boiling done as follows: in 120 gall copper put the grouts of say 80 lbs cochl fill the copper up with aq to within a foot of the top, make it boil, add 3 lbs pearlash, boil 6 hours, add 1½ lbs al draw fire & leave till next day.

993. Next day draw off & strain into 90 gall butt, it is then fit to be precipitated but it is better to leave it a week for the liquor to redden, ultimately precipitated with 5¼ galls zinc sulphur diluted with 5¼ galls water

994. Take 3 more boilings of grouts & serve as [992-3]

995. Take 3 more boilings of grouts & serve as [992-3]

996. Take 3 more boilings of grouts & serve as [992-3]

997. Take 6 x 6 lbs cochl (AJ & Co Oct/57 at 3/11 lbs)

Each 6 lbs treated as usual with 12 oz sub carb pot (salts of tartar) 6 oz al & precipd 3 x 6 lbs boilings together with 4½ lbs cr tart at 150°

Draw off the supernatant liquor & filter the settled colour which was converted into 36 galls lake precipitate liquor of the strength 1 lb coch = 1 galls

998. Take the 36 galls lake precipitate liquor as [997] dissolve it with 4 lbs pearlash in 2 galls hot water & strain, stir 2 or 3 times during the day, leave till next day

999. Stir up [998] & syphon it into the precipd purple [992-996] stirring well all the time & for some period afterwards to ensure a perfect mixture, strain, filter, press & dry off at a strong heat which will prevent mouldings

Notes: Generally the batch of grouts (say from 80 lbs cochl) is boiled 3 consecutive times as [992] reducing the materials to half the quantity each time

Notes: Let the precipitates be well washed in the 90 galls butt before the liquor [998] was added  
The supernatant was left alkaline

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<sup>47</sup> Marginal number from URC P1P250AL01 (Carmine. The H:O: Quality):

“748. Water in large copper to within 3½ inches of top as described [580] add 20 lbs mex cochl (black), add immediately 20 oz cit: acid & boil 15 min, strain & leave the liquor 2 hours as [580].”

<sup>48</sup> Marginal number from URC P1P317AL01 (Ruby Carmine):

“889. 120 gallon copper of well settled water is made to boil then cooled down to 180°. Add 1¼ lbs sub carb potash, add 20 lbs cochineal, boil or nearly for 15 minutes, add 5 lbs bi tart potash, boil for 10 minutes longer, add 1¼ oz powd alum, boil 5 minutes, draw fire, strain into 90 gall butt.”

## Appendix 5. Elemental analysis of reconstructions and historical samples

**Table 29.** Elemental analysis of the reference of carminic with aluminium, reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes and historical samples.

| Chromophore | Name                 | $\mu$ EDXRF*                             | ICP-AES / mg g <sup>-1</sup> |      |      |      |
|-------------|----------------------|------------------------------------------|------------------------------|------|------|------|
|             |                      |                                          | Al                           | Ca   | B    | Zn   |
| Lake CA-Al  | CA-Al                | K, P, S, Fe                              | 39.4                         |      |      |      |
| Lake HOC    | HOC                  | Ca, K, S, Fe                             | 7.07                         |      | 6.27 |      |
| Lake FOC    | FOC                  | <b>Ca</b> , K, S, Cl                     | 14.8                         | 27.6 | 2.79 |      |
|             | FOC W&N              | <b>Ca</b> , Fe, K, P, S                  | 13.0                         | 20.3 | 0.57 |      |
|             | Carmin LF            | <b>Ca</b> , Sn, Fe, Mn, Ba, S, P         | 29.7                         | 38.8 | 0.18 |      |
| Lake FPC    | FPC                  | <b>Ca</b> , K, S, Fe                     | 11.8                         | 52.1 |      |      |
|             | FPC W&N              | <b>Ca</b> , K, Fe, P, S                  | 17.7                         | 26.9 |      |      |
|             | CrimAl <sup>#</sup>  | <b>Ca</b> , S, K                         | n.a.                         | n.a. |      |      |
|             | CrimCa               | <b>Ca</b> , <b>S</b> , Fe                | 4.16                         | 244  |      |      |
|             | Crim W&N             | <b>Ca</b> , <b>S</b> , Fe, Ba            | 13.9                         | 84.2 |      |      |
|             | Scarlet <sup>#</sup> | <b>Hg</b> , <b>S</b> , <b>Ca</b> , Fe, K | n.a.                         | n.a. |      |      |
| Lake Purple | Purple <sup>#</sup>  | <b>Zn</b> , K, Ca, S                     | n.a.                         | n.a. |      | n.a. |
|             | Purple W&N           | <b>Zn</b> , <b>Ca</b> , Sn, S, Fe, Mn    | 4.70                         | 76.7 |      | 20.2 |

\* Elements in significant amounts, associated with the pigment's matrix, are presented in bold. The remaining elements were detected in small amounts and are associated to contributions of the dyestuff raw material (K, Fe, S, Cl, P, Ca) and to the oil paint tubes (Sn, Mn, Ba).

<sup>#</sup> Even though the reconstructions CrimAl, Scarlet and Purple were not analysed with ICP-AES, aluminium was assumed to be present due to the addition of alum and subsequent precipitation of pigment during the manufacturing processes.

n.a. Not analysed.

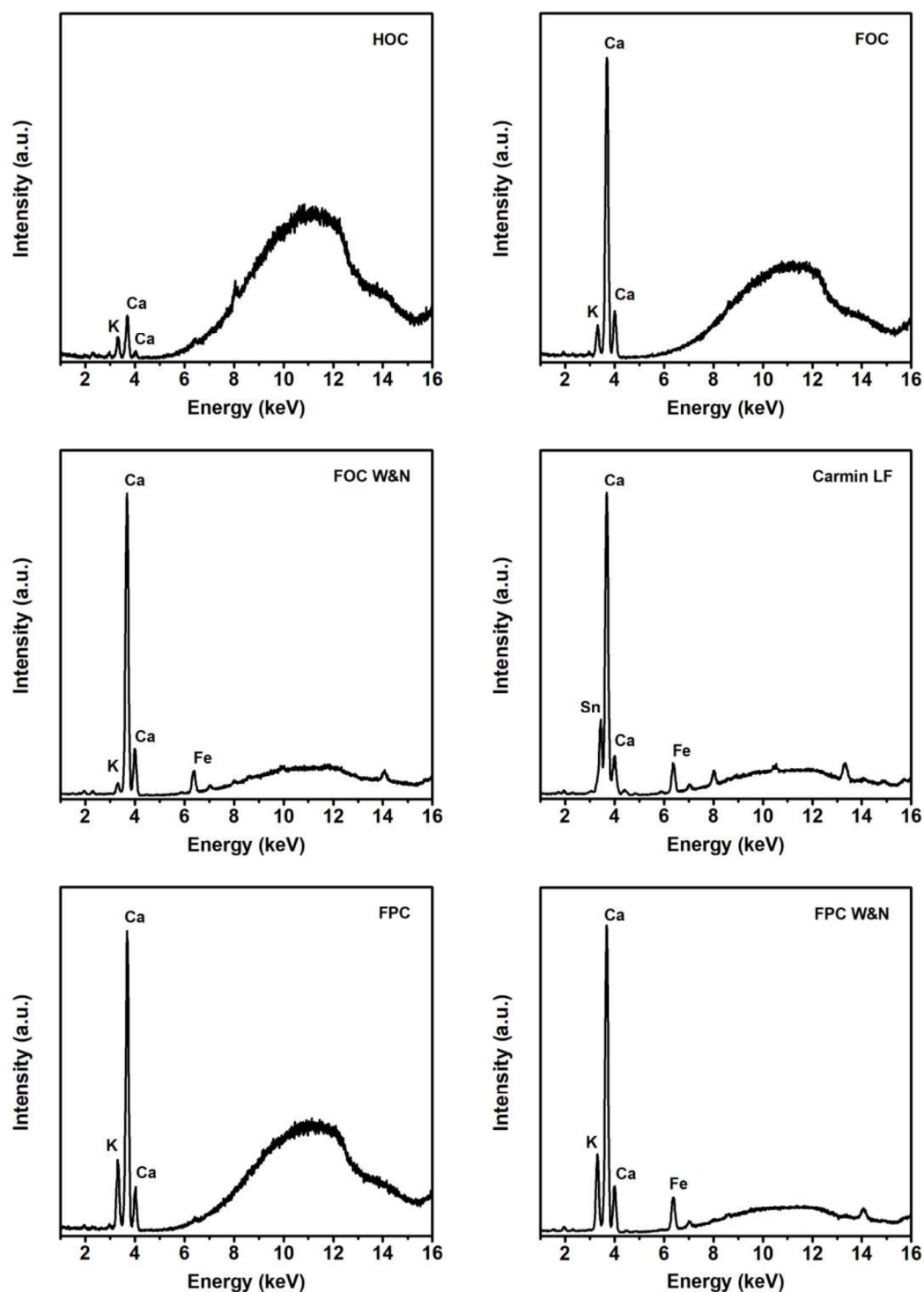


**Figure 51.**  $\mu$ EDXRF spectra of reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes and historical samples.

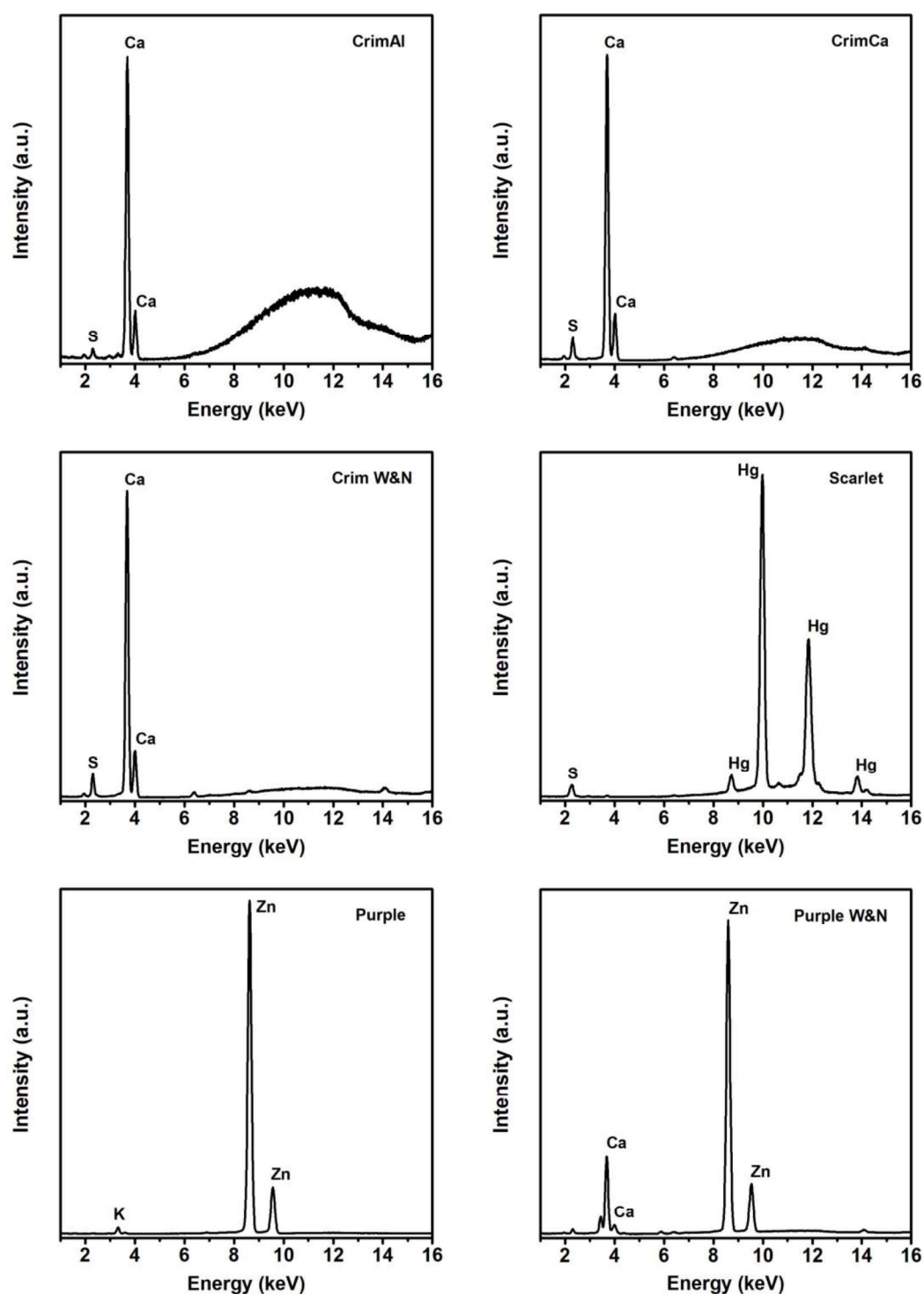


**Figure 52.**  $\mu$ EDXRF spectra of reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes and historical samples.

## Appendix 6. Reflectance spectra of reconstructions and historical samples before and after the accelerated light ageing experience

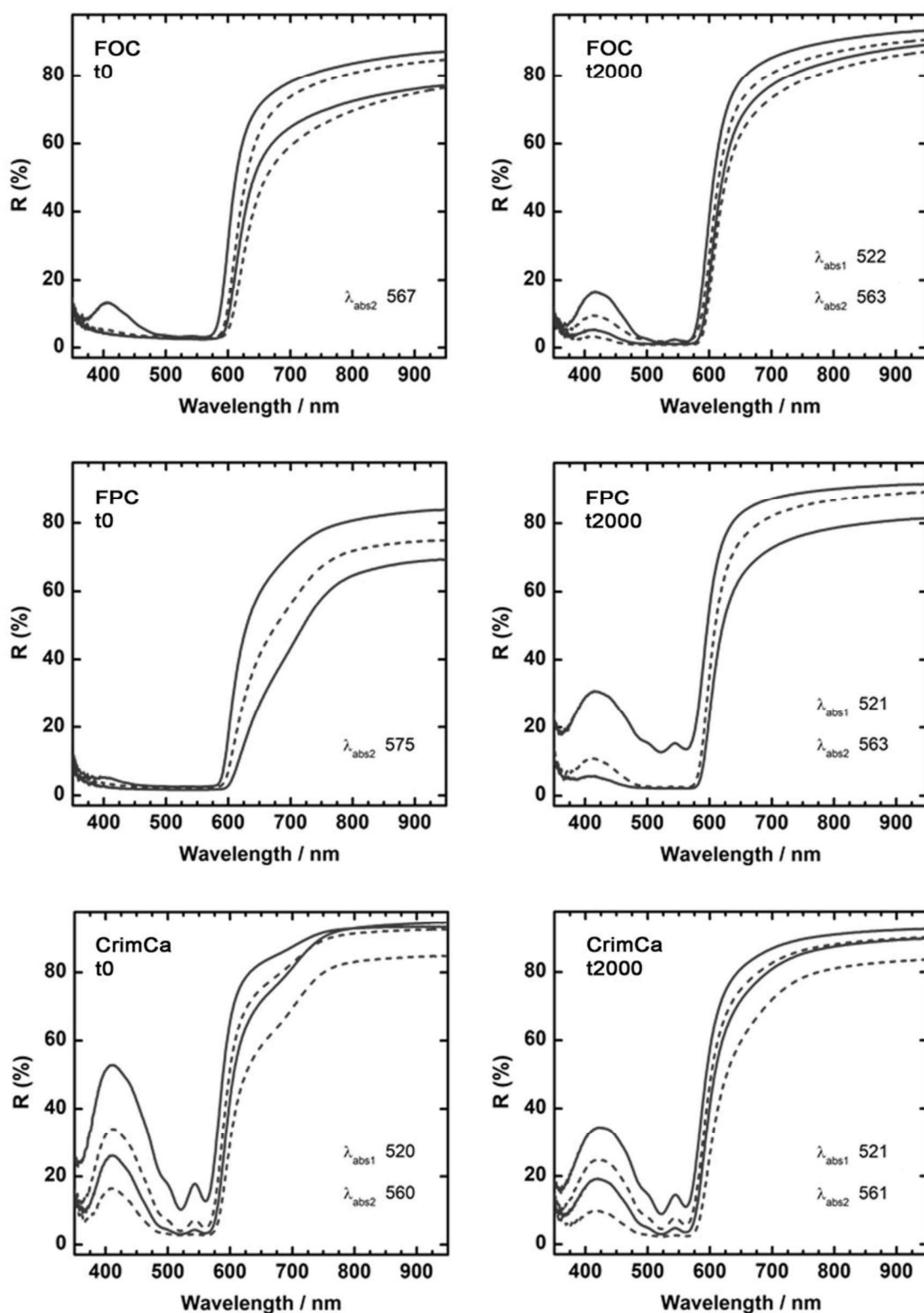


**Figure 53.** Reflectance spectra of reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes with gum-arabic before (t0) and after (t2000) the accelerated light ageing experience.

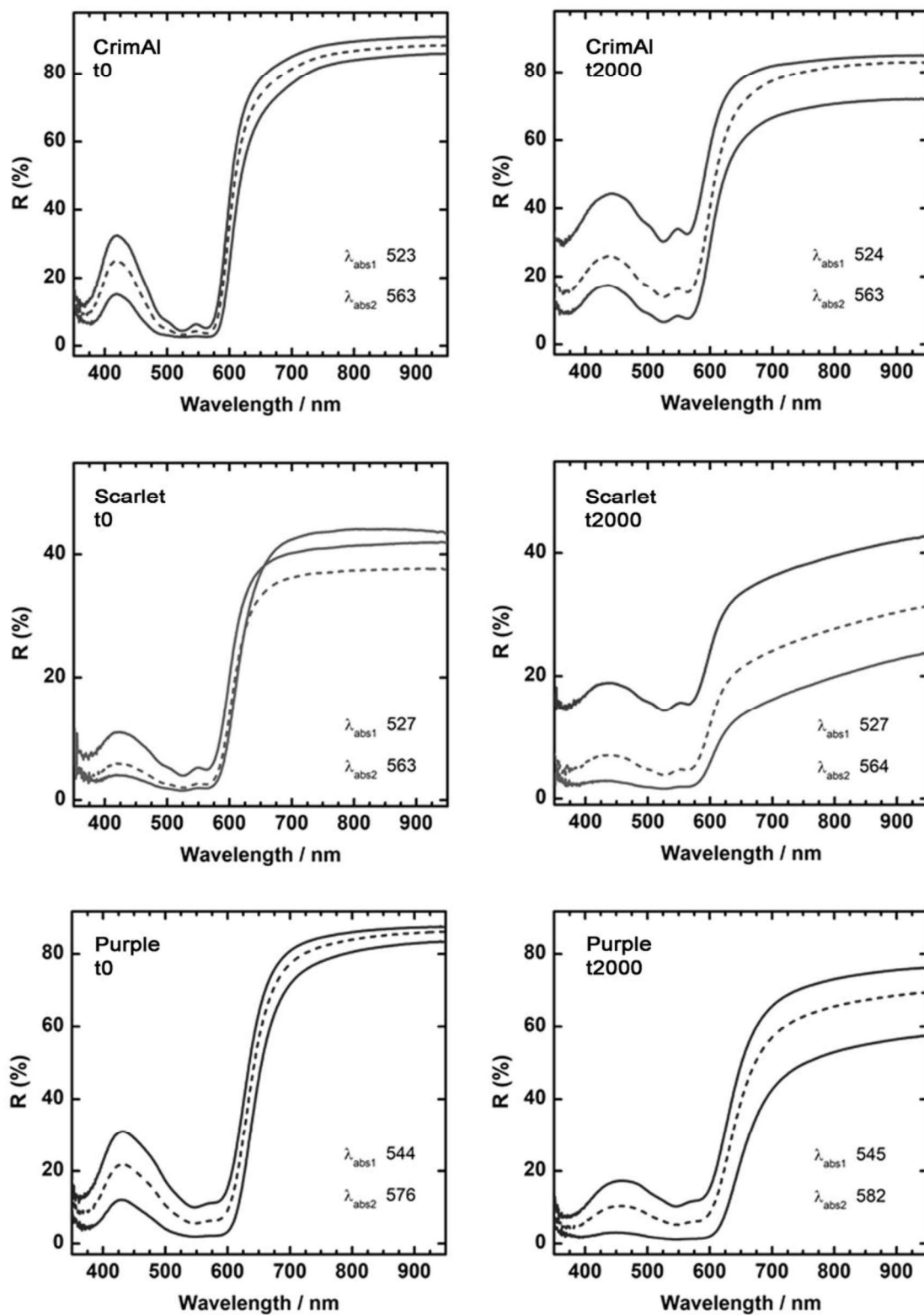


**Figure 54.** Reflectance spectra of reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes with gum-arabic before (t0) and after (t2000) the accelerated light ageing experience.

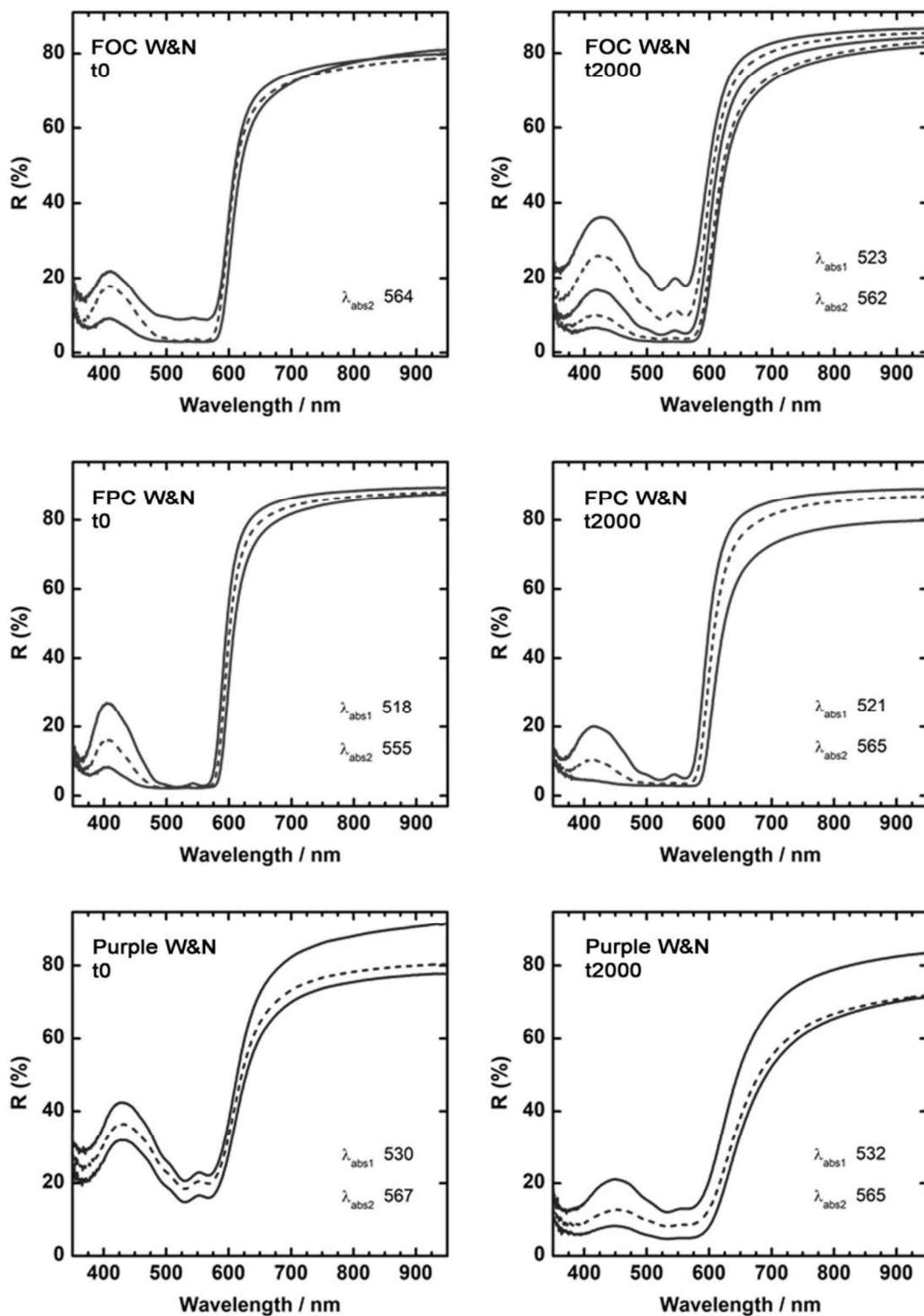


**Figure 55.** Reflectance spectra of historical samples with gum-arabic before (t0) and after (t2000) the accelerated light ageing experience.

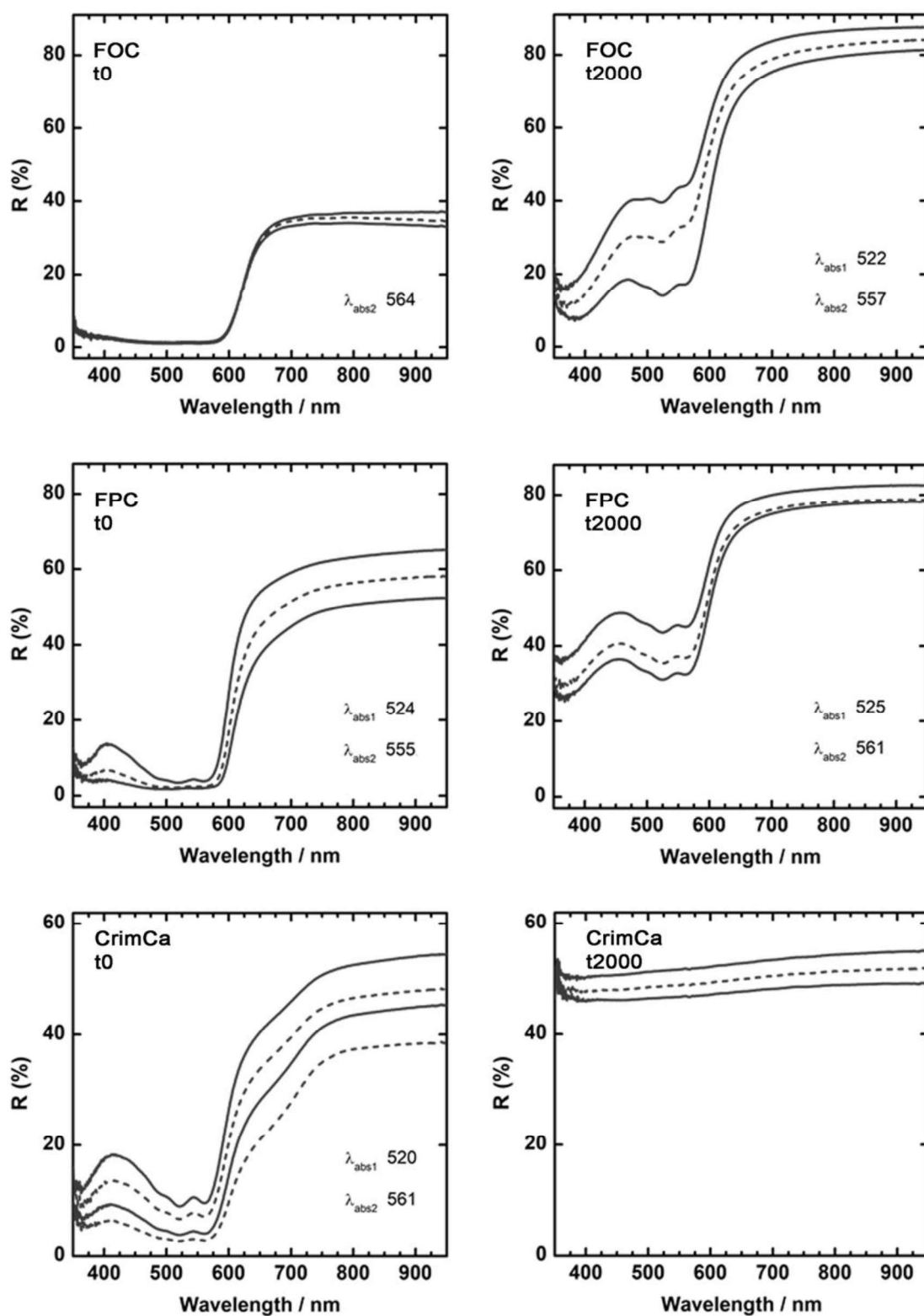


**Figure 56.** Reflectance spectra of reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes with PVAc before (t0) and after (t2000) the accelerated light ageing experience.

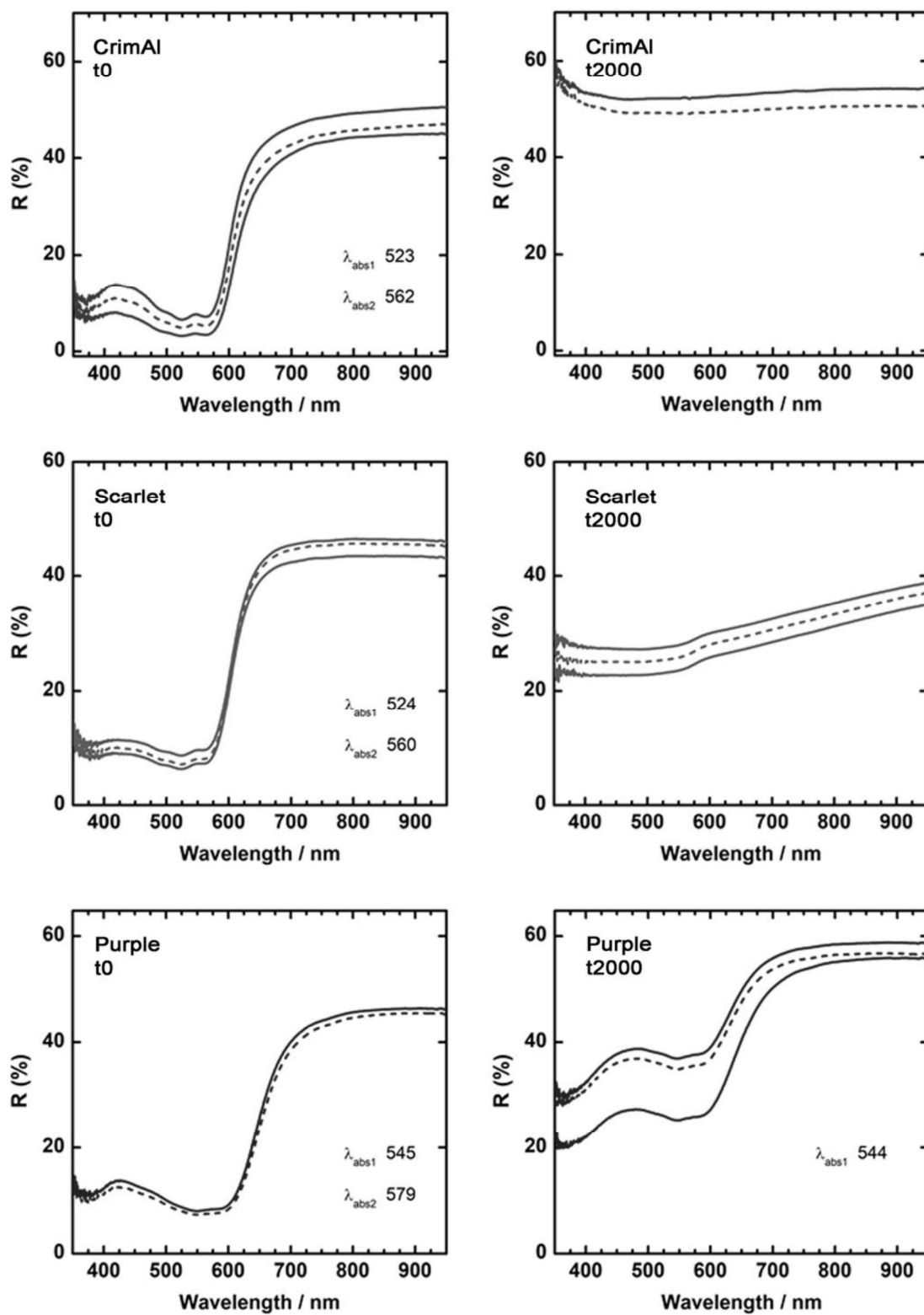


**Figure 57.** Reflectance spectra of reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes with PVAc before ( $t_0$ ) and after ( $t_{2000}$ ) the accelerated light ageing experience.

## Appendix 7. Infrared spectra of reconstructions before and after the accelerated light ageing experience

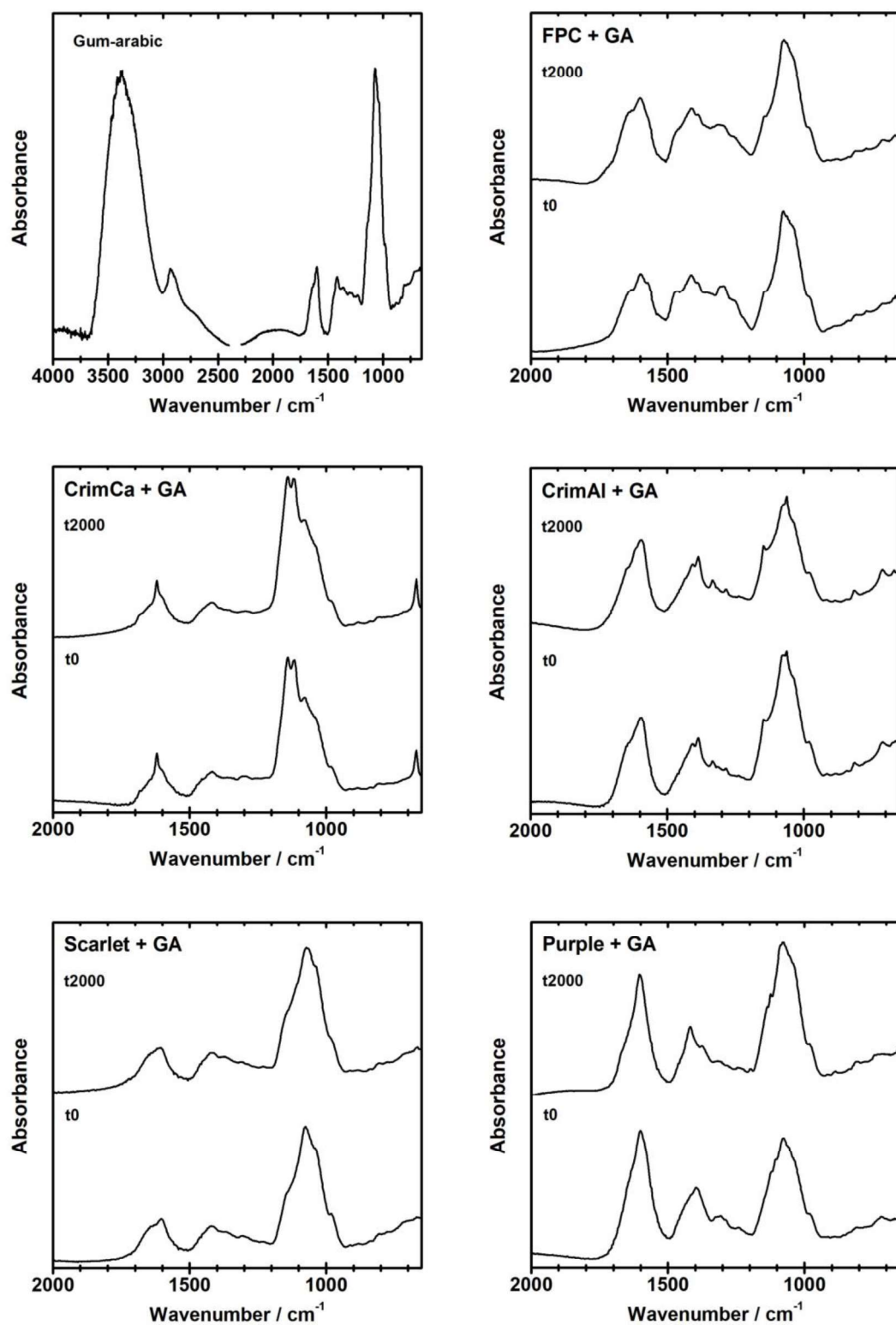


**Figure 58.** Infrared spectra of gum-arabic 10% and of reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes with gum-arabic before ( $t_0$ ) and after ( $t_{2000}$ ) the accelerated light ageing experience.

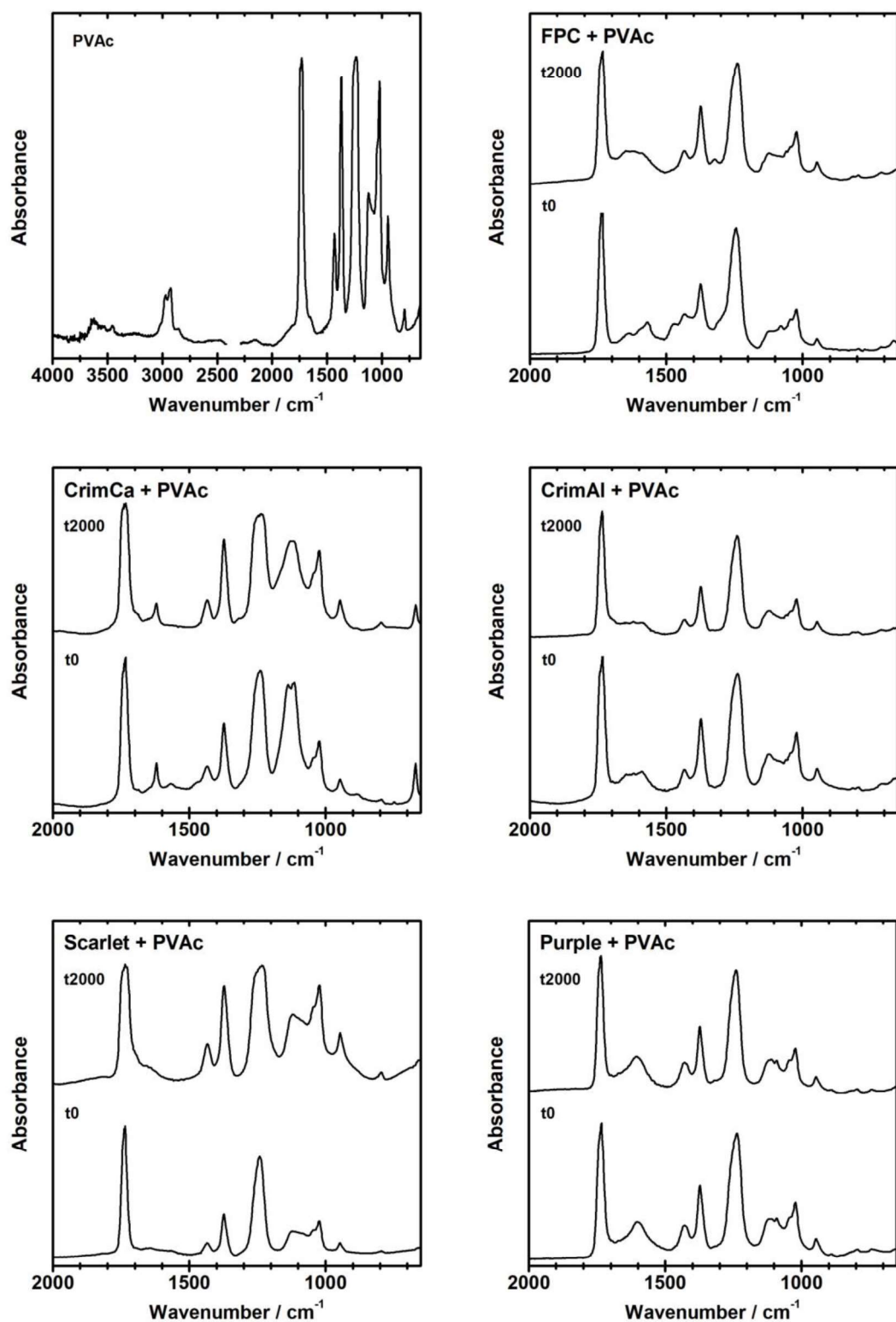


**Figure 59.** Infrared spectra of PVAc 20% and of reconstructions of cochineal lake pigments prepared from W&N's manufacturing processes with PVAc before (t0) and after (t2000) the accelerated light ageing experience.

## Appendix 8. Microfading curves of reconstructions and historical samples

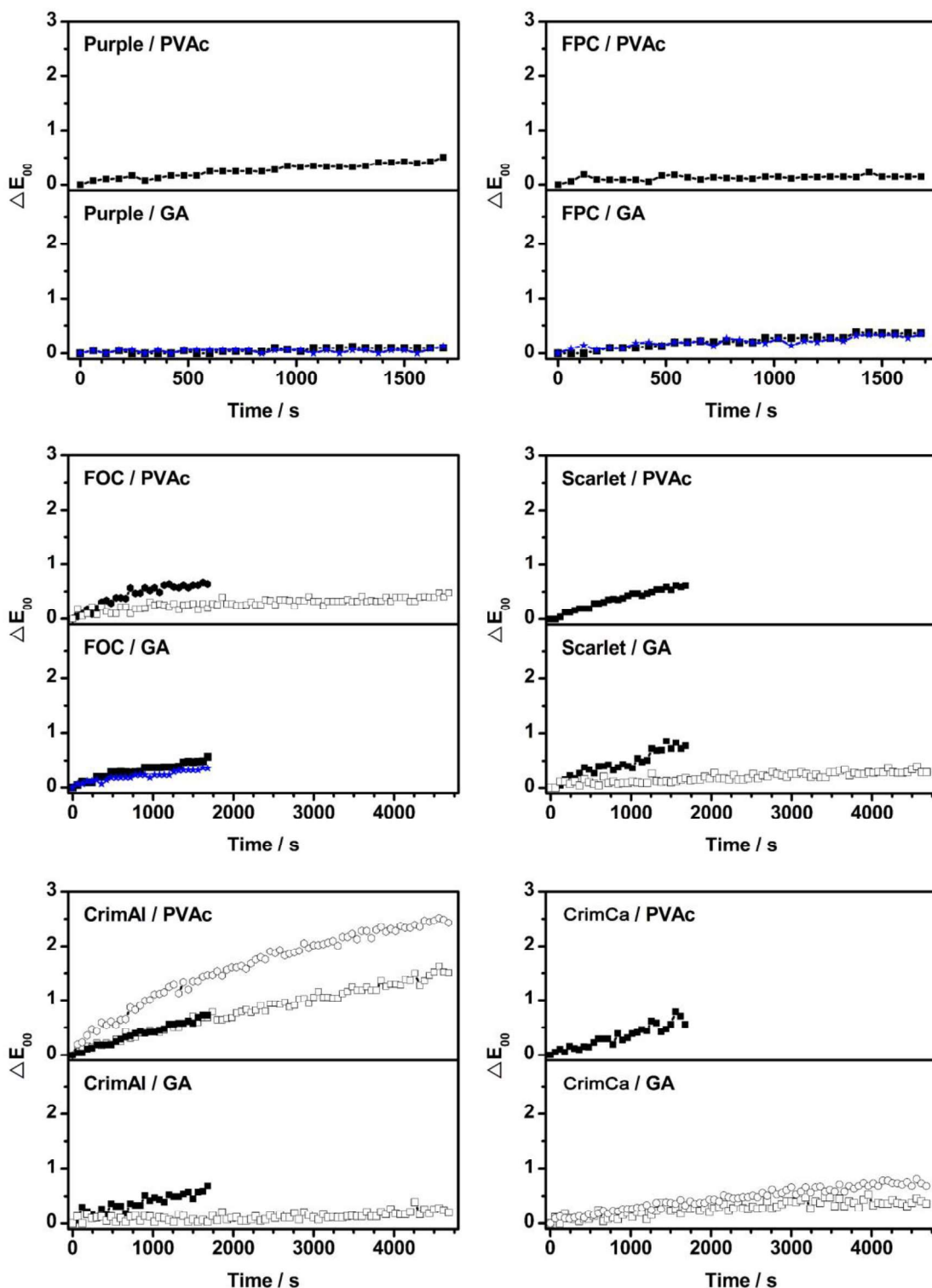


**Figure 60.** Microfading curves obtained for cochineal paints after 28-minute (1680 s), black curves, and 78-minute (4680 s), white curves, exposures to an illumination intensity of 3.3 Mlx. Blue curves refer to the historic samples Purple W&N, FOC W&N and FPC W&N.

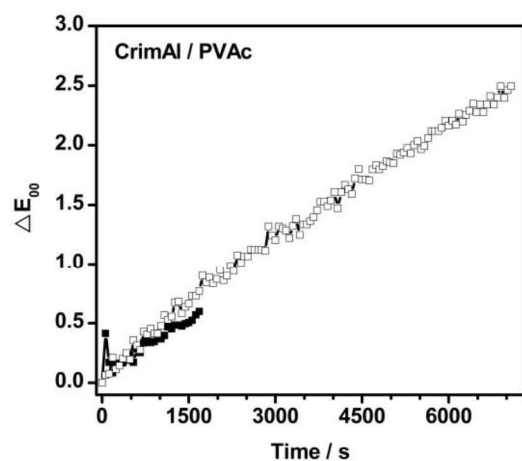


**Figure 61.** Microfading curves obtained for cochineal paint after 28-minute (1680 s) and 118-minute (7080 s) exposures to an illumination intensity of 4.3 Mlx.

## Appendix 9. Standard deviation of the reflectance average spectra extracted from ROIs

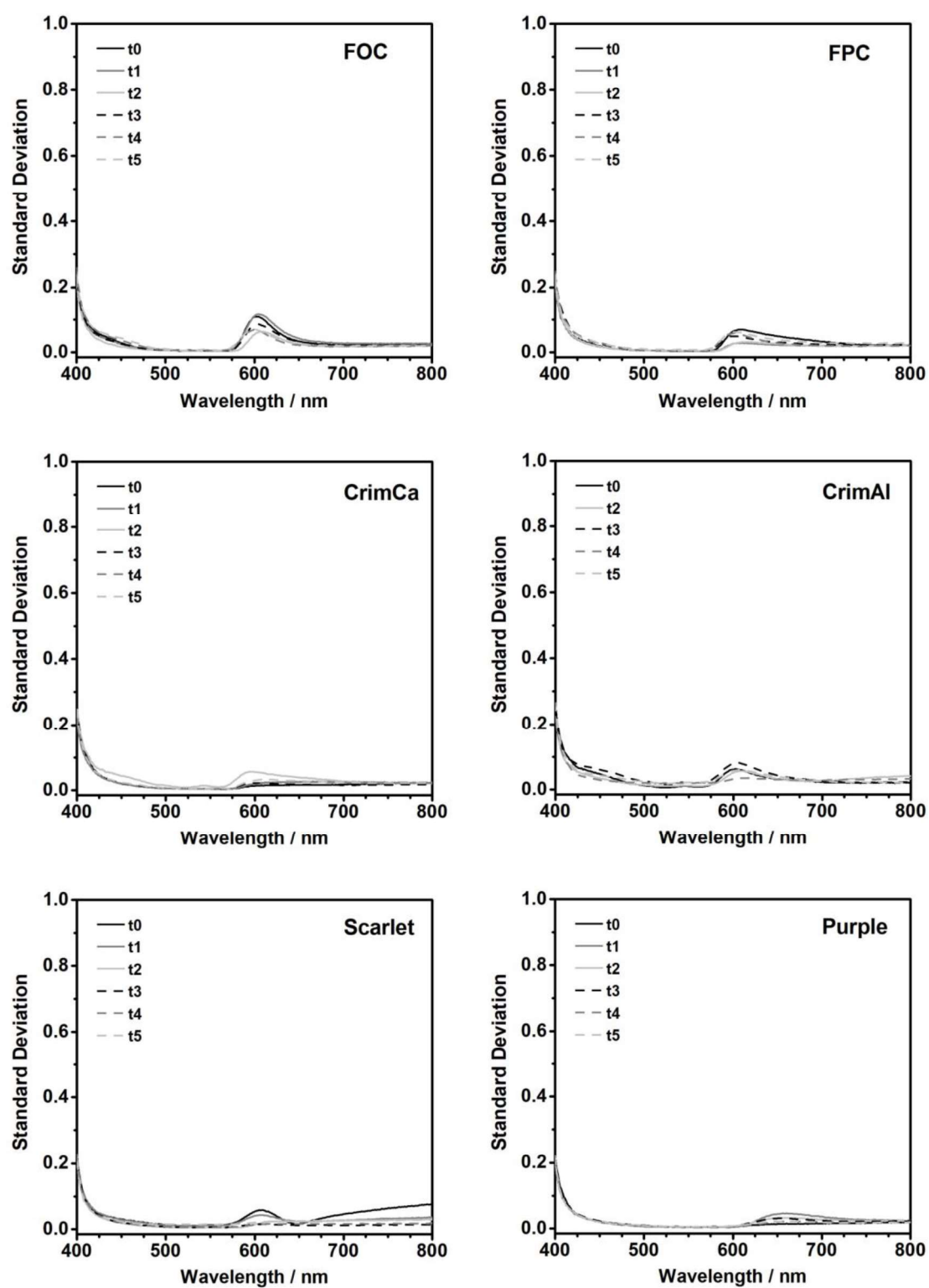


**Figure 62.** Standard deviation of the reflectance average spectra extracted from ROIs of cochineal references with gum-arabic subjected to the accelerated light ageing experience (Figure 44).

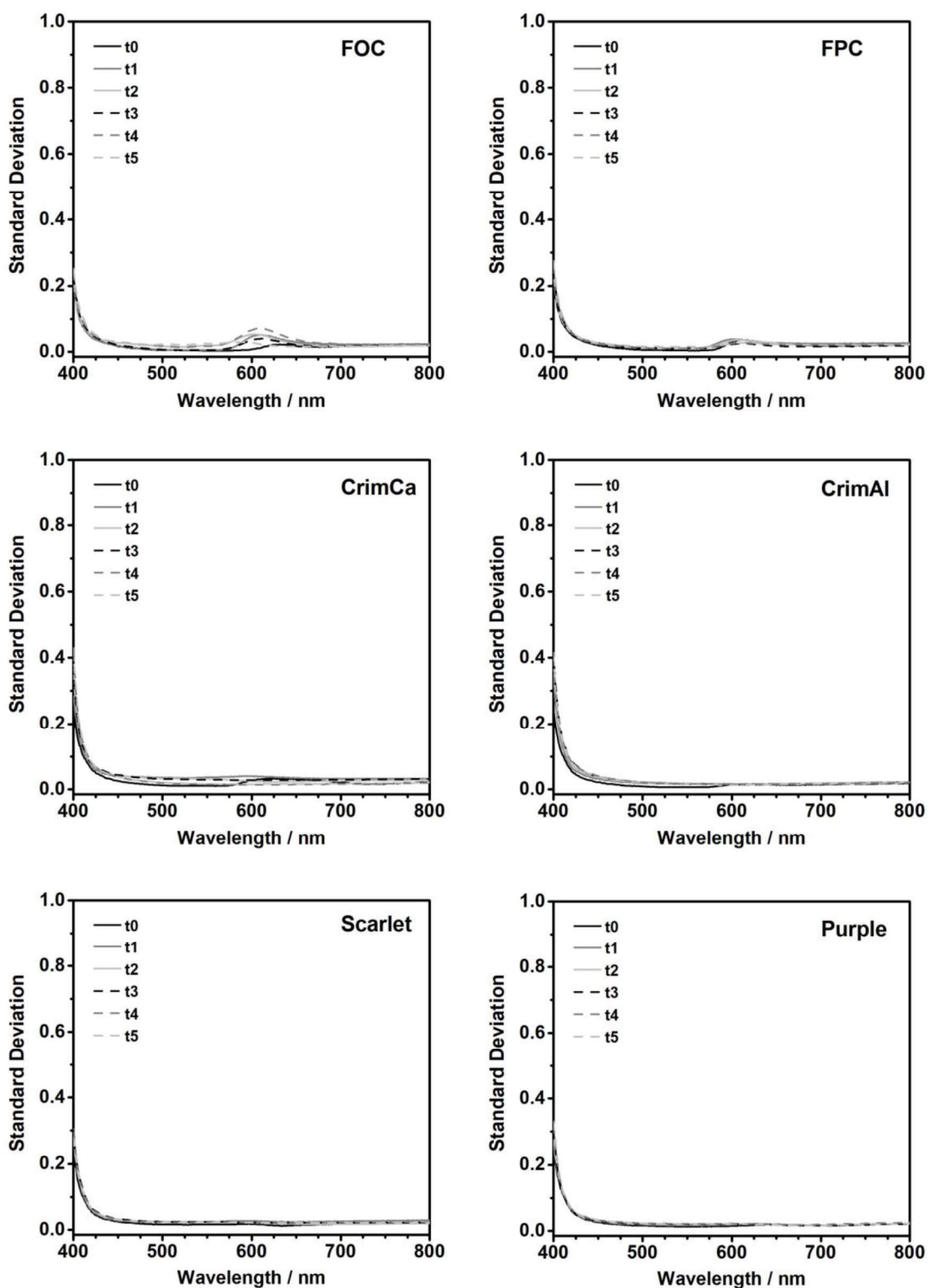


**Figure 63.** Standard deviation of the reflectance average spectra extracted from ROIs of cochineal references with PVAc subjected to the accelerated light ageing experience (Figure 45).

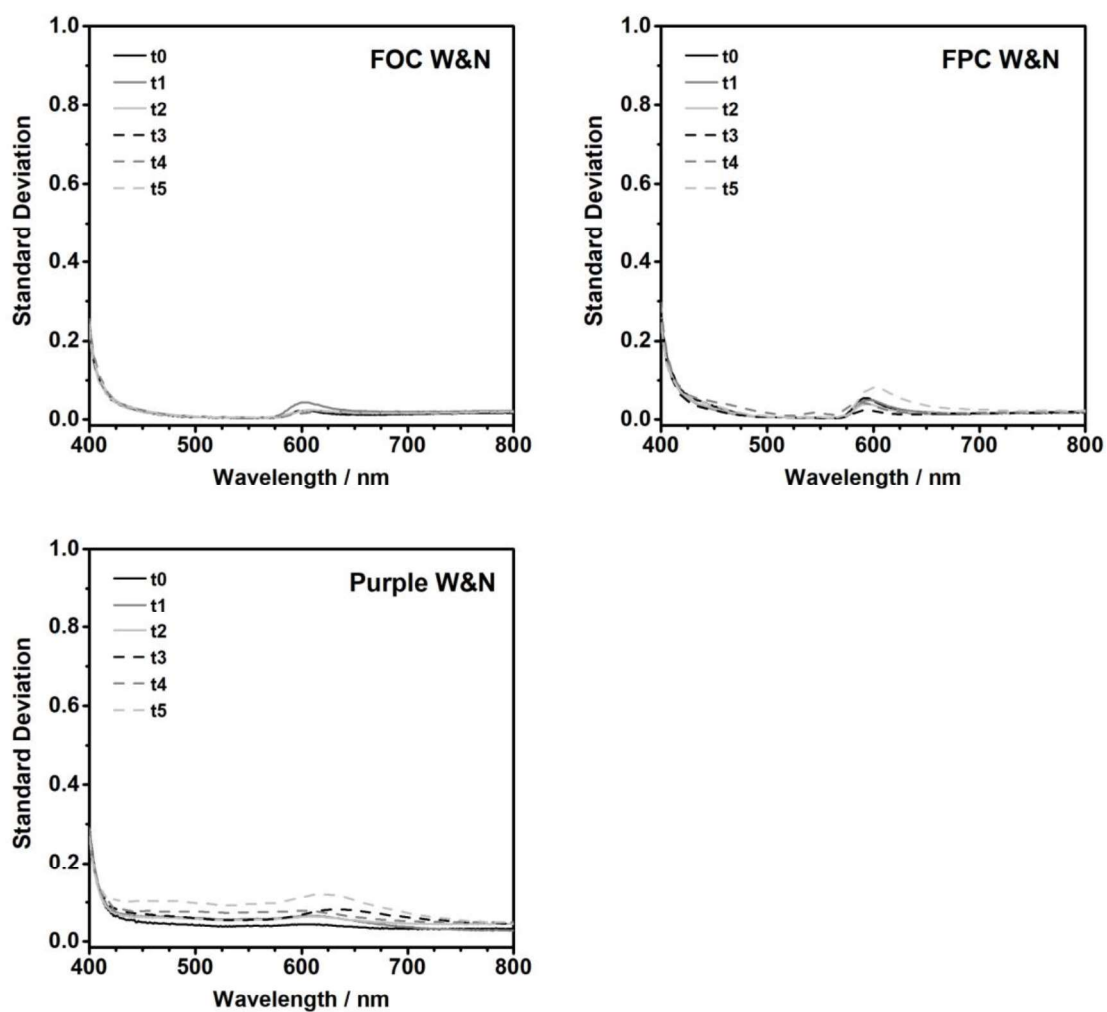


**Figure 64.** Standard deviation of the reflectance average spectra extracted from ROIs of cochineal historical samples with gum-arabic subjected to the accelerated light ageing experience (Figure 46).

