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Historical Stained Glass Painting Techniques
Technology and preservation

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Francisco

My little BIG warrior.

"As Freud once said, «one day, in retrospect, the years of struggle will strike you as the most beautiful»

Mark Manson

RESUMO

O presente trabalho teve como objetivo o estudo das técnicas de pintura aplicadas ao vitral, nomeadamente grisalha, *sanguine*, e esmaltes azuis. Foram também realizados ensaios de corrosão em amostras de esmalte azul reproduzidas, de pigmento e de pintura, de forma a melhor compreender os mecanismos de corrosão envolvidos. Foi efetuada uma pesquisa e interpretação de diversos tratados históricos, datados entre os séculos XII e XVIII, com o estudo da produção e tecnologia das técnicas de pintura mencionadas, desde a preparação do pigmento até à preparação da pintura. Para o efeito, foram caracterizadas matérias-primas utilizadas na produção de esmaltes azuis, seguindo-se a reprodução de esmaltes azuis, *sanguine* e grisalha, a partir de receitas históricas previamente selecionadas. Foram considerados vários parâmetros a ter em conta durante a sua produção, nomeadamente temperatura de cozedura, moagem do pigmento, e ligante (componente orgânico que permite a adesão da pintura ao substrato) a utilizar na preparação da pintura. A metodologia selecionada para a caracterização das amostras consistiu na utilização de diversas técnicas analíticas para um estudo químico e morfológico das mesmas. Os resultados obtidos foram comparados com três coleções de vitrais Portuguesas, do Mosteiro de Santa Maria da Vitória na Batalha, Charola do Convento de Cristo em Tomar e do Palácio Nacional da Pena em Sintra.

O presente estudo permitiu concluir que a escolha das matérias-primas para a produção do pigmento, a seleção do ligante a utilizar, e a temperatura e taxa de variação de aquecimento terão impacto no resultado final obtido, resultando em camadas pictóricas com maior adesão ao substrato vítreo. A utilização de *zaffre* (mistura de cobalto calcinado e areia) como agente colorante não permite determinar *a priori* qual a cor final da pintura, ao contrário da adição de *smalt* (vidro azul de cobalto) como agente colorante. Relativamente aos estudos de corrosão, os ensaios de imersão efetuados às amostras em pó de esmalte azul permitiram verificar que com a lixiviação dos iões alcalinos, os iões Co^{2+} serão influenciados por outros iões presentes na matriz vítrea. Em alguns casos, verificou-se que os iões Pb^{2+} foram os responsáveis pela alteração da cor, com a formação de carbonato de chumbo hidratado, resultando na alteração da cor do pigmento. Relativamente à pintura com *sanguine*, foi possível concluir que o resultado final obtido é fortemente influenciado pela taxa de variação de aquecimento. Concluiu-se também que a utilização de goma-arábica como ligante, ou como ingrediente no pigmento, resulta numa maior adesão da camada pictórica ao substrato vítreo. Relativamente à pintura a grisalha, foi possível concluir que existiu uma evolução da morfologia da pintura com um aumento da sua homogeneidade.

Os resultados obtidos para as reproduções efetuadas mostraram uma boa correlação com os resultados obtidos para as amostras históricas, evidenciando a importância do cruzamento das fontes históricas com o trabalho laboratorial.

Palavras-chave: vitral, pintura, esmaltes, sanguine red, grisalha, Portugal

ABSTRACT

The aim of this project is the study of the painting techniques applied on stained glass, namely blue enamels, sanguine red and grisaille. The research and interpretation of several historical treatises dated to between the 12th and the 18th centuries was performed, with a study of the production technology of the selected painting techniques, from the preparation of the pigment to the preparation of the paint. With this in mind, selected raw materials used in the productions of blue enamels were characterized, followed by the reproduction of selected historical recipes of blue enamels, sanguine red and grisaille. Parameters such as firing temperature, grinding and binding agents used to apply the paint on glass were considered. The methodology selected was based on the chemical and morphological characterization of both reproduced powder and paint samples by means of a multi-analytical approach. In addition to the reproduction of the selected painting techniques, corrosion studies of blue enamel powder and paint samples were performed in order to provide new insights on the corrosions mechanisms involved. The results obtained were compared with selected painted stained-glass fragments from Portuguese collections, mainly the ones located in Batalha Monastery, Charola from Convento de Cristo in Tomar and Pena National Palace in Sintra.

The present study concluded that the choice of the raw materials to the production of the paint, the binder used to apply the paint, and parameters such as firing temperature and heating rate, had an impact on the outcome, resulting on a better adhesion of the paint layer to the base glass. The use of zaffer as a colouring agent does not allow determination of the outcome of the paint, while adding powdered glass such as smalt gives to the glass painter the opportunity to know the final result before firing. As for sanguine red paint, it is concluded that the final outcome of the paint is strongly influenced by the heating rate. In addition, the use of gum arabic as a binder, or in the pigment itself, provides a better adhesion of the paint layer to the base glass. Regarding the grisaille painting, the main differences between the recipes lay on the composition of the lead-based glass and on the ratios between this and the colouring agents. Furthermore, it was also possible to conclude that there is an evolution of the morphology of the grisailles towards a higher homogeneity of the surface.

The corrosion studies performed on blue enamels allowed to conclude that with the lixiviation of the alkaline components of the enamel, cobalt will be influenced by other neighbouring ions, leading to a change of colour. In some cases, Pb^{2+} ions may also be the responsible for this colour change, with the formation of lead white.

The results obtained were in a good agreement with the characterization of the selected case studies, evidencing the importance of the intersection between the written sources and the laboratory work.

Keywords: stained glass, painting, enamels, sanguine red, grisaille, Portugal

PUBLICATIONS

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Machado, A. and Vilarigues, M. (2018) 'Blue enamel pigment – chemical and morphological characterization of its corrosion process', *Corrosion Science*.
DOI: https://doi.org/10.1016/j.corsci.2018.05.005.

Machado, A. *et al.* (2017) 'Swiss Kabinettscheiben from a 19th century Portuguese collection. Study and chemical characterisation', in Wolf, S. and Pury-Gysel, A. de (eds) *Annales du 20e Congrès de l'Association International pour l'Histoire du Verre, Fribourg/Romont, 7-11 Septembre 2015*. Romont: AIHV - Association Internationale pour l'Histoire du Verre, pp. 684–688.
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Machado, A. *et al.* (2017) 'Swiss Stained-Glass Panels: An Analytical Study', *Microscopy and Microanalysis*, 23(4), pp. 878–890.
DOI: https://doi.org/10.1017/S1431927617000629.

Machado, A. and Vilarigues, M. (2016) 'Cobalt blue - reproduction and characterisation of blue enamel recipes from The Handmaid to the Arts by Robert Dossie', *Glass Technology: European Journal of Glass Science and Technology Part A*, 57(4), pp. 131–140.
DOI: https://doi.org/10.13036/17533546.57.4.027.

Vilarigues, M. and Machado, A. (2015) 'Pintar com luz: o esmalte azul na pintura de vitral', *Química*, 137, pp. 31–35.
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μ-EDXRF - – micro - Energy Dispersive X-ray Fluorescence spectroscopy

μ-PIXE - micro - Particle Induced X-ray Emission

BSE – Backscattered Electron imaging

EDS – Energy Dispersive Spetroscopy

FORS – Fibre Optics Reflectance Spectroscopy

FTIR – Fourier Transform Infrared Spectroscopy

HLLA – High Lime Low Alkali

ICP-AES - Inductively Coupled Plasma Atomic Emission Spectroscopy

PNP – Pena National Palace

SEM – Scanning Electron Microscopy

VCR – Vitrocentre Romont

XRD - X-ray Diffraction

INTRODUCTION

Einen Glasmaler heißt man mich
In die Gläser kann schmelzen ich
Bildwerk manch herrliche Person
Adelig Frauen und Mann
Samt Iren Kindern abgebildet
Und Ihres Geschlechts Wappen und Schilt
Dass man erkennen kann darben
Wann das Geschlecht herkommen sei.

Jost Amman, *Panoplia Omnium Artium* (The Book of Trades), 1568

I was sixteen years old when in an Art History class we opened our books on the chapter concerning the Gothic period, and I remember being amazed by an impressive view of the interior of the Saint Chapelle, laid out in the first two pages. In 2015, during the Corpus Vitrearum meeting in Paris, I had the opportunity to visit the Saint Chapelle for the first time, and the feeling was ten times stronger. Many wrote about stained glass, but one must witness its splendour to understand the meaning of the words. Stories were told through a game of light and shadow, with coloured and colourless glass decorated with painted motifs, depicting the stories that the Bible could not transmit to the illiterate (Figure 1). The glass-painter played a significant role to tell these stories. The meaning of "glass-painter", as well as his role and importance in the creation of a stained-glass window, slowly emerged during the course of the centuries. Theophilus, in his 12th-century treatise *De diversibus artibus* demonstrates that the work was developed within a workshop. Glazier was a term coined to those who worked on all aspects of window making, thus it was expected that the glass-painting process was also assigned to the glazier.

Figure 1 – Saint Chappelle, in Paris, is an example of the employment of stained glass windows in Gothic architecture. The set of stained glass panels is dated between the 13th and the 15th centuries, presenting 19th-century repairs. © Andreia Machado.

The term "glass-painter" appeared for the first time between the end of the 15th century and beginning of the 16th century (Brown and O'Connor, 1991). Eventually, the division of tasks between the glazier and the glass-painter became more acute: to the glazier was reserved the work of assembling the painted glass fragments and leading the window, while the glass-painter was in charge of the artistic side of the stained glass making (Brown and O'Connor, 1991). In fact, this division is notorious already in the 14th century, as we can attest by Cennino Cenninis' *Il Libro dell'Arte*, when in chapter CLXXI he writes:

"It is true that this occupation is not much practiced by our profession, and is practiced more by those who make a business of it. And ordinarily those masters who do the work possess more skill than craftsmanship, and they are almost forced to turn, for help on the drawing, to someone who possesses finished craftsmanship, that is, to one of all-around, good ability. (…) And he gives to you a colour which he makes from well-ground copper-fillings; and with this colour, (…) you shape up your shadows gradually, matching up the arrangement of the folds and the other details of the figure, on one piece of glass after another…"

This passage demonstrates that the glass-painter was involved in the outline of the composition, shadows and other details. The process of fusing the paint was controlled by the glazier. Cenninis' words do demonstrate this division of tasks, but also a disregard towards glass painting (Thompson, 1954; Baroni, Brun and Travaglio, 2013). Despite this clear division between the craftsman and the artist, glass painting was still considered less important when compared with panel painting. As Sarah Brown and David O'Connor wrote, "it is profoundly ironic that outstanding glass-painters, working in a medium

which after all is concerned with light, should end up in relative obscurity." (Brown & O'Connor 1991, p. 4).

This panorama shifts between the 15th and beginning of the 16th century when many glass-painters begun to be acknowledged by their work; the increase of demand for small-scale stained-glass panels most likely contributed to this event (Figure 2) (Brown and O'Connor, 1991).

Figure 2 – Published in 1568, Jost Amman's *Panoplia Omnium Artium* (The Book of Trades) presents a woodcut representing a glass-painter working in his studio[6].

This recognition coincides with the moving of many glass-painters throughout the European territory to fulfil new commissions. As an example we have Luis Alemão (*Alemão* as "German" in Portuguese, a name certainly associated with his origin), who appears designated as a glass-painter in three documents dated to between 1446 and 1450, from Batalha Monastery, in Portugal (Hess, 2000).

The interest in stained glass slowly decreased during the 18th century, and many stained-glass panels were replaced by clear glass, with few surviving in their original location (Giesicke and Ruoss, 2000). This interest was rediscovered in the 19th century with the publication of several texts and treatises on stained glass and its painting techniques. From the 14th century and during the Renaissance period, the publication of manuscripts increased, especially in the 16th century, reaching a culmination point during the 17th and 18th centuries. The oldest "systematic publications" known about glass, glass paints and stained glass are the ones by Antonio Neri (1612) and André Félibien (1676) (Caen, 2009). Many other treatises were published, preserving the knowledge of ancient glass painters, combining them with the technologies available.

[6] https://commons.wikimedia.org/wiki/File:Glasmaler-1568.png, accessed in October 2017.

Over the last years we have been witnessing an increasing enthusiasm on rediscovering the old techniques used by glass-painters. Several studies have already been made concerning historical stained-glass production techniques in the Middle Ages, with an important publication by Sebastian Strobl – *Glastechnik des Mittelalters* (1990) –, which approaches the production of glass and glass painting during this period, linked with the information provided by the manuscripts. (Strobl, 1990). Karine Boulanger made a compilation of the technical treatises of the Medieval Period up to the 15th century, which deal with stained glass and stained-glass painting (Boulanger, 2004). Regarding the study and reproduction of stained-glass paints, two important works are worth mentioning: *Antoine de Pise, l'art du vitrail vers 1400*, edited by Claudine Lautier and Dany Sandron (2008), and *The production of stained glass in the county of Flanders and the duchy of Brabant from the XVth to the XVIIIth centuries: materials and techniques*, by Joost Caen (2009). The first is an important study of the 14th-century treatise *Memoria* written by Antonio da Pisa, unveiling the complexity of the chemical composition of the colours apart from the interpretation of the treatise (Lautier and Sandron, 2008), while the second is an investigation on several stained-glass collections from Flanders studying the development of the enamel and sanguine red techniques, with the reproduction of blue enamels according to their chemical composition (Caen, 2009). These works contributed to an accurate translation of the recipes, important to understand the mains steps of stained-glass paint production. Currently, two on-going international projects are focused on the transmission the technique and its translation in practical recipes. The ARTECHNE project, led by Sven Dupré on a collaboration between the Utrecht University and University of Amsterdam, combines both "humanities and historical disciplines with laboratory work". The "Making and Knowing Project", led by Pamela Smith from Columbia University, explores the "relationship between the laboratory work as we know today and the craft workshops of the past, on an intersection between artistic making and scientific knowing".

The study and characterization of stained glass in Portugal has been a subject of interest from many years. We can say that the modern historiography on the Portuguese stained-glass panorama began in 1827 with the publication *Memoria Historica sobre as Obras do Real Mosteiro de Santa Maria da Vitória*, written by D. Francisco de S. Luis, where the author mentions the poor conditions of the stained glass of Batalha Monastery. Carlos Barros published in 1983 *O vitral em Portugal, Séculos XV-XVI*, dedicated to the collection of Batalha, and with reference to other stained-glass panels located at Setúbal, Viana do Alentejo and Vila do Conde (Barros, 1983). The research in stained glass in Portugal was later carried by Pedro Redol who published in 2003 a complete historic and iconographic study of the stained-glass collection of Batalha Monastery (Redol, 2003). The research on Portuguese stained-glass has been also developed at Vicarte and Department of Conservation and Restoration during these past 15 years by Márcia Vilarigues and her team. Archaeometric studies on stained glass and stained-glass painting of the Batalha collection were undertaken, and corrosion studies on the degradation mechanisms on medieval glass and the development of new cleaning solutions (Vilarigues and Da Silva, 2004;

Vilarigues and da Silva, 2006, 2009, Vilarigues *et al.*, 2009, 2011; Machado, Redol and Branco, 2011; Delgado *et al.*, 2015, 2017). Later on, the finding of the stained-glass assemblage in Tomar allowed its historic and chemical characterization, and also a historic, iconographic and archaeometric comparison with the 16th-century stained-glass group of Batalha was established (Delgado *et al.*, 2011; Vilarigues, Delgado and Redol, 2011). Recently, the stained-glass collection of Pena National Palace has been studied in detail from historical, archival, analytical and preservation perspectives, under the project "The Stained glass collection of King Ferdinand II of Portugal – Assembling the puzzle" (Martinho and Vilarigues, 2011, 2012; Rodrigues *et al.*, 2014; Rodrigues and Martinho, 2015; Coutinho *et al.*, 2016).

A detailed knowledge of the materials used by the artists is essential to unveil their techniques and to place their works in a technical and historical context, as well as to establish adequate conservation procedures. To achieve this goal, one must be aware of the production technology and the "know-how" which was transmitted throughout time. When it comes to stained-glass painting, this relation between the written sources and the laboratory work has not received an in-depth study.

The present thesis aims to contribute with new knowledge on the paint materials applied in stained glass. Three of the main painting techniques were approached in this work – enamels, sanguine red, and grisaille –, with special emphasis on enamel paint and in particular the colour blue. The blue colour was considered due to the many challenges that present when related to other coloured enamels from coeval period. With this in mind, a chemical and morphological characterization of blue enamel paint was undertaken. An approach to the production of sanguine red and grisaille paint was also performed. Silver staining was not considered on this work since its production technology does not result on a painted surface *stricto sensu*.

The key points covered in this work are:

- Research and interpretation of historical recipes;
- Identification and characterization of selected raw materials used in the production of blue enamel paint;
- Study of the production technology of paints, from the preparation of the pigment to the preparation of the paint, including reproduction of historical paint recipes;
- Chemical and morphological characterization of the reproduced paints, both in powder form and painted on glass.
- Corrosion studies of selected blue enamel powder and painted samples.

The results obtained were compared with selected painted stained-glass fragments from Portuguese collections, mainly the ones located in Batalha Monastery, Charola from Convento de Cristo in Tomar and Pena National Palace.

The work is divided into five chapters. Chapter one presents an introduction of the three painting techniques approached in this study: grisaille, enamels and sanguine red, with a brief context and definition of each paint, followed by an approach of the conservation issues related to these paints.
Chapter two presents a historic context of the three Portuguese collections.
Chapter three deals with the historic treatises on stained glass and stained-glass painting. This chapter is divided into two sections, spanning the periods before and after the publication of *L'Arte Vetraria* by Antonio Neri (1612), the first published work about glass: sub-chapter 3.1 concerns the late antique, medieval and pre-modern manuscripts from the Greek and Roman period until the 16th century; sub-chapter 3.2 treats the publications from the 17th and 18th centuries and also includes comments on two important 19th-century publications.
Chapter four describes the methodology, the process, and the results for each of the painting techniques studied, with special attention paid to blue enamels. The comparison with the case studies is also presented.
Finally, the overall conclusions of this work are presented, providing an outlook of the research which is still required concerning each of the painting techniques, and also questions which appeared during the course of this study.

With this thesis I hope to contribute for a better understanding of the technology behind these stained-glass painting techniques, and of the deterioration mechanisms related to blue enamels, and to raise awareness to this amazing heritage present in our country.

CHAPTER 1

THE HISTORY AND TECHNOLOGY OF STAINED GLASS PAINTING TECHNIQUES

As described by Pedro Redol in his publication dedicated to the stained-glass collection of Batalha Monastery, stained glass can be defined as a group of glass pieces, colourless, pot-metal, or as an application of two pieces of glass, with or without paint. The glass pieces are united by a lead came, which is welded by a lead and tin alloy (Redol, 2003, p. 61).

In the Middle Ages, the art of stained glass flourished with the construction of cathedrals, reaching its peak in the 13th century during the Gothic architecture (Brisac, 1989). The aesthetics of light introduced by Abbot Suger, with the construction of St. Denis also contributed to its growth. During the Romanesque period, the walls were the support of the building's structure. With the arrival of the Gothic architecture and the introduction of new architectural elements such as flying buttresses, walls were torn down to make room for monumental stained-glass windows. It was not only a complement to the architecture but also a symbolic path between God and believers.

Stained-glass painting was, from the beginning of the craft, one of the processes which experienced many changes and developments. The grisaille painting was the first painted decoration ever to be used on stained glass. This paint was applied to depict on coloured and clear glass figures, motives and other details as a thick opaque line, known as *grisaille à contourner*, or as a thin line, known as *grisaille à modeler* (Caen, 2009; Schalm *et al.*, 2009). After the arrival of yellow silver staining, it was also used for shadows and other details of the composition. Examples of 17th-century stained glass reveal the high-quality compositions that could be obtained using only the grisaille (Figure 1.1).

The grisaille can be defined as a black or brown product, obtained by the mixture and grinding of metallic oxides (such as iron or copper) and a fluxing agent, with a vehicle charged with a certain amount of binder (Debitus, 1991; Verità, 1996). This paint is applied to the front side of the stained-glass panel. Some examples of the application of the grisaille on the back side can be found, such as the 15th-century stained-glass donor panel from Waterperry Church in Oxford (Brown & O'Connor 1991, p. 59).

(a) (b)

Figure 1.1 – The grisaille painting followed the development of the painting on stained glass, allowing the creation of very detailed compositions with the use of grisaille. A portrait, dated to the 16th century (Portugal) (a), and Zabulon, dated to the 17th century (Low Countries) (b), are two examples which can be found in the collections from Convento de Cristo, Tomar, and Pena National Palace, Sintra, respectively.

The treatise *De coloribus et artibus romanorum*, written by Eraclius between the 10th and the 13th centuries, indicates the mixture of a lead-rich glass with iron filings. Brass, a Cu-Zn alloy, could also be added to the base glass. At the present moment, there is knowledge of only two stained-glass collections that present grisaille painting with a significant amount of zinc, one of them is the 16th-century stained-glass collection located at Batalha Monastery, and the other is the 16th century stained-glass collection located at *Salvatorkirche*, in Munich (Marschner, 1996; Vilarigues, 2008). The 12th-century treatise *De diversibus artibus* by Theophilus prescribes a mixture of a lead-rich glass with copper fillings. To apply the grisaille, wine, urine, or gum arabic were used as binders. The paint is heated at temperatures between 600 ºC and 750 ºC, allowing the attachment of the paint layer to the base glass, with a complete fusion of lead and the decomposition of some of the oxides, with the releasing of the metals which remain in its solid state dispersed in the glassy matrix (Verità, 1996; Vilarigues and Da Silva, 2004). This melting process results in a proper fusion of the paint, creating a diffuse interface between the grisaille and the base glass (Carmona, Villegas and Navarro, 2006; Machado *et al.*, 2017). The result is an opaque layer with an uneven surface (Figure 1.2). The quality of the grisaille will, thus, depend on the thickness of the paint, the correct amount of binder, and the firing temperature (Caen, 2009).

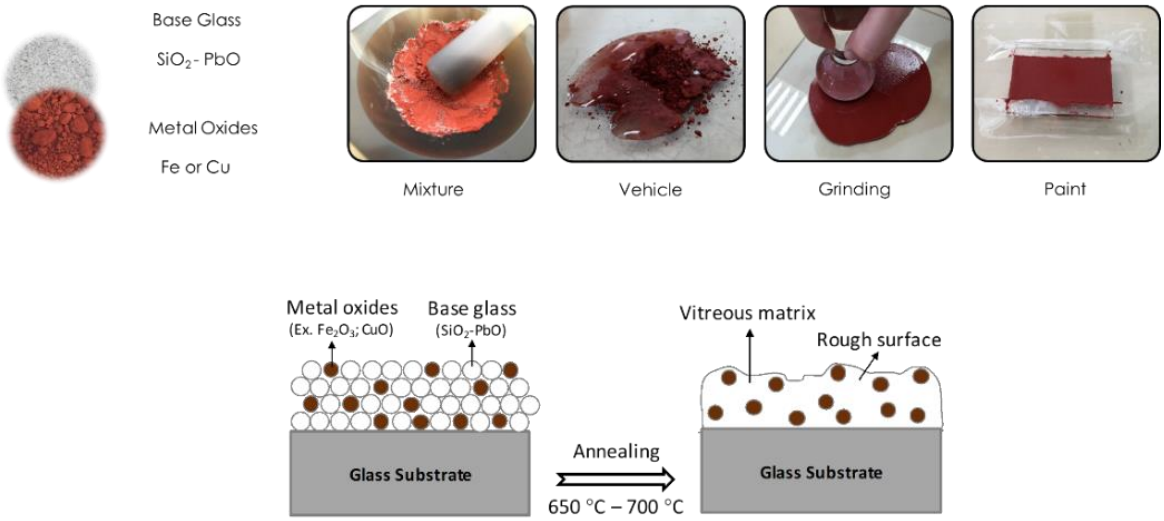


Figure 1.2. – Schematic representation of the production of a grisaille paint.

The grisaille painting together with the application of silver staining (from the 14th century onwards) remained until the beginning of the 15th century the only painting technique used in stained glass (Strobl, 1990). Yellow silver staining consists on the application of a diluted silver salt with a binder, such as gum arabic, usually on the backside of the stained glass panel. The paint is heated at temperatures between 500 ºC and 650 ºC (Verità, 1996). The yellow colour is provided by the penetration of the Ag^+ ions in the glass matrix by ion exchange with K^+ and Na^+ ions, and reduced to Ag^0, forming clusters of silver nanoparticles of various sizes, between 10 and 200 nm (Jembrih-Simbürger *et al.*, 2002; Delgado *et al.*, 2011). From this point on, coloured glass was slowly being superseded by clear glass, onto which was applied the paint (Raguin, 2008; Caen, 2009). The application of coloured enamels was the highpoint of this tendency. In the words of Peter van Treeck, "the stained glass window became a picture" (Treeck 2000, p. 57). The use of enamel painting became widespread, led by Switzerland and the Netherlands (Figure 1.3). Stained-glass painting reached its apogee between the 16th and 17th centuries (Giesicke and Ruoss, 2000). The production of domestic stained glass, which arose in Central Europe in the beginning of the 15th century, was also fundamental for the use of enamels. Stained glass painters came up with the necessity to create more complex "pictorial compositions", for which grisaille and yellow silver staining were not sufficient (Strobl, 1990).

Figure 1.3 – *The Last Supper* (PNP2855), a stained glass panel from the Low Countries dated to the 17th century, is a perfect example of the employment of colourful enamels in combination with the application of grisaille, yellow silver staining and sanguine.
© Luis Pavão, Parques de Sintra Monte da Lua, S.A.

One of the first examples where we can see the application of enamels in stained glass is in the diptych of Maarten van Nieuwenhove, dated to 1487 by Hans Memling. The background of the diptych presents windows with stained glass roundels painted with blue enamels (Figure 1.4). The first known written evidence (until today) of recipes for enamel painting is a 16th-century treatise, known as the Antwerp Manuscript (from the Plantin-Moretus museum collection, M. 64), with recipes for blue, green and purple enamels (Caen, 2009).

Figure 1.4 – Diptych of Maarten Nieuwenhove, dated to 1487, located at the Memlingmuseum in Bruges.
© Web Gallery of Art.

An enamel can be defined as a glass that melts at a lower temperature than the glass to which it is applied (Schalm *et al.*, 2009). It is usually applied on the front side of the stained glass panel. It is composed of a base glass, a colouring agent and a binder. Both base glass and colouring agent are mixed together and melted at high temperatures. While fused, the glass is poured into cold water creating a thermal shock, which breaks the glass into several chunks. These pieces of glass are ground into a fine powder to mix with a binding agent, such as gum arabic or an essential oil. After firing the paint, at temperatures between 600 ºC and 700 ºC, the result is a homogeneous layer of enamel over the glass that can be opaque or more translucent. The thickness of the enamel layer can vary between 10 µm and 100 µm. Unlike the usual results obtained for the grisaille, the interface between the enamel layer and the base glass is usually sharp (Schalm *et al.*, 2009; Machado *et al.*, 2017) (Figure 1.5).

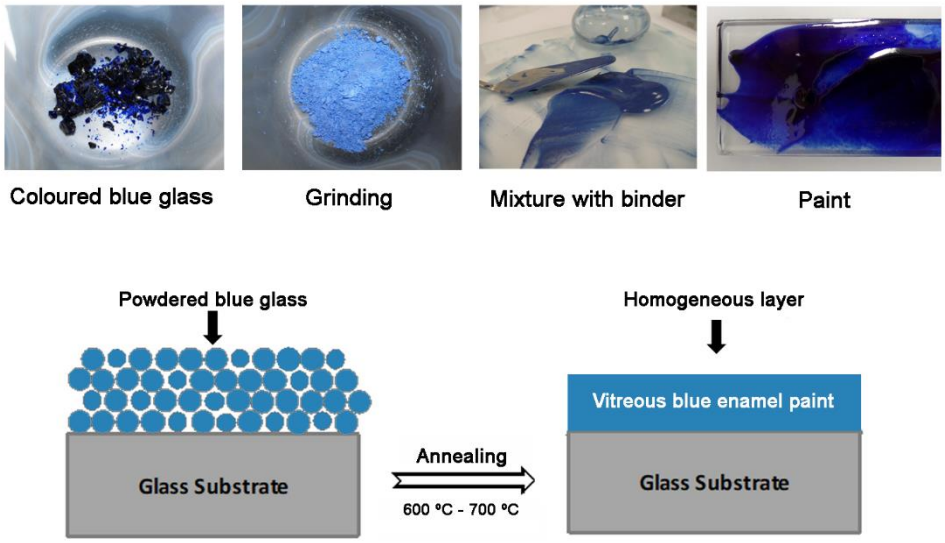


Figure 1.5 - Schematic representation of the production of a blue enamel paint.

Contemporary with enamel paint, sanguine red was used as a translucent or opaque paint, applied on both front and backside of the stained glass panel. Its application in stained glass began probably in the second half of the 15th century (Caen, 2009). Opaque sanguine could be used mainly to represent architectural features (e.g. marble or brick), or in heraldry, and translucent sanguine was used mainly for carnations. Two examples of the application of both translucent and opaque sanguine red are represented in Figure 1.6.

(a) (b)

Figure 1.6 – Two examples of the application of sanguine red: (a) *The Parable of the Good Samaritan* (PNP2871), a production from the Low Countries dated to the 17th century, and (b) stained glass roundel *Elena Schrader*, dated probably to the 18th century. © Luis Pavão, Parques de Sintra Monte da Lua, S.A., © Fernanda Barroso.

Recipes show that the main pigment used for this type of paint was iron oxide, in the form of hematite (α-Fe_2O_3). Anhydrous oxides can produce a range of colours from black through shades of purple and red. Particle size and shape influences the final colour obtained. For the red colour, iron particles present a diameter between 0.1 µm and 0.5 µm (Schwertmann and R. M. Cornell, 2000). Antonio Neri in his treatise *L'Arte Vetraria* (1612) writes about how to make *Crocus Martis* (the alchemical name for red iron oxide obtained from the oxidation of iron or steel), saying "this way causes the glass to appear a rather bright blood red" (Engle 2003, p. 34). Other authors such as Johann Kunckel and Pierre Le Viel present various translations and recipes for the production and application of this pigment. Besides the presence of iron red, other components could be added such as lead, *rocaille*[7] (lead glass), antimony or bismuth. To apply the paint, a mixture of the pigment with a "watered gum arabic" is prescribed in the written sources, such as Pierre Le Vieil's 18th-century treatise *L'Art de la Peinture sur Verre et de Vitrerie* (Vieil 1774, p. 195).

Sanguine can thus be defined as a mixture of red iron oxide, as a mineral or obtained by the oxidation of iron filings, with gum arabic and water. As referred above, the pigment can also be mixed with other components such as lead-base glass, antimony, and bismuth. The paint is fired at temperatures between 600 ºC and 700 ºC (similar to the enamels), resulting on a thin layer of a homogeneous and smooth paint, opaque or more translucent according to the amount of paint applied (Figure 1.7).

[7] *Rocaille* is a term to refer a lead-rich glass, already used for the production of grisaille painting. This term first appeared in the 17th century treatise *Recueil des Essaies des Merveilles de la Peinture* by Pierre Le Brun (1635).

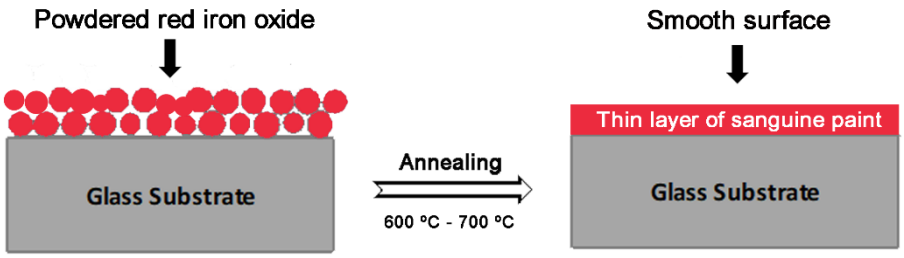
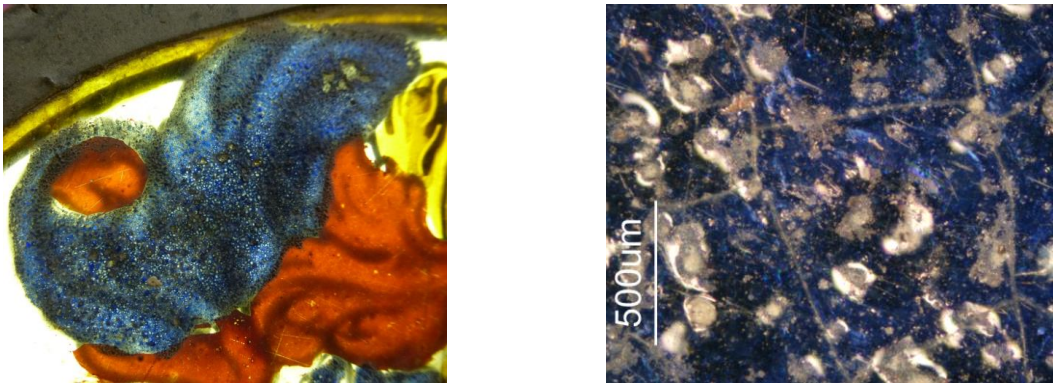


Figure 1.7 - Schematic representation of the production of a sanguine red paint.

Stained-glass paint, whether is referred to grisaille, sanguine or enamels, can present many conservation issues. They can be related to external factors such as relative humidity and temperature variations, to the way of applying the paint by using the incorrect proportion of pigment:binder, to adhesion problems between the paint layer and the base glass, to the heating conditions, such as low firing temperature and a high annealing rate, or inherent to the composition of the paint layer (Figure 1.8).



(a) (b)

Figure 1.8 – (a) Detail of a blue enamel painting and (b) optical microscopy image of a 17th century stained glass fragment from a stained-glass panel from Ajuda National Palace, presenting conservation problems, namely a fractured surface. This can either be caused by incompatibilities between the enamel layer and the base glass or by the heating conditions of the enamel layer © Fernanda Barroso.

Figure 1.9 – In this 17th century (?) stained-glass fragment (PNP2534) located at the Nobble Hall of Pena National Palace, the detachment of the blue enamel paint from the base glass is visible.
© Andreia Machado.

In the present work, the corrosion of blue enamel powder and paint samples was studied, due to the conservation problems that this colour can present when compared to other enamels of the same period (Schalm *et al.*, 2009). Previous studies have been conducted in order to access degradation mechanisms, among which the formation of micro-cracks dividing the surface of the paint layer, due to different thermal expansion coefficients between the enamel and the base glass, or a degradation of the latter conducting to a detachment of the paint layer (Van der Snickt *et al.*, 2006; Schalm *et al.*, 2009) (Figure 1.9). Studies also indicate a relation between the micro-cracks and the thickness of the enamel layer. In some cases, the enamel layer can be intact, but cross-sections of the samples show cracking of the base glass underneath (Attard-Montalto and Shortland, 2014).

With this in mind, it becomes relevant to study the preparation of blue enamel paints and its application, so that we may plan new conservation approaches.

CHAPTER 2

STAINED GLASS IN PORTUGAL – THE CASE STUDIES

Three important Portuguese stained-glass collections are the centre of this chapter. The first collection is located in Santa Maria da Vitória Monastery in Batalha and is dated to between the 15th and 16th centuries. Batalha is home of the oldest Portuguese stained-glass panels known until today. The 15th-century group is characterized by clear glass painted with grisaille motives, together with coloured glass pieces. The 16th-century group presents a more figurative style and is of a higher quality in terms of the glass and glass paint. It shows a combination of grisaille and silver stain (Redol, 2003).

The second case study concerns the recently discovered stained-glass assemblage from the Convento de Cristo in Tomar, which was found during two conservation interventions in 1999 and 2009 and is dated from the 16th century. It is characterized by the presence of glass fragments painted with grisaille and silver stain, the latter with shades varying between yellow and orange. The glass has a high quality, and its production location is still uncertain (Vilarigues et al. 2011).

The third case study regards the stained glass collection from Pena National Palace in Sintra. It includes stained-glass panels from Switzerland, Germany, and the Low Countries. The collection is dated to between the 14th and 19th centuries. They exhibit a technique of high-quality, with the presence of grisaille, silver stain, enamels and sanguine red.

According to what we know so far, the history of stained glass in Portugal begins in the 15th century, later when compared with other countries such as France, Germany or England. It was with the King João I (1383-1433) that Portugal gained an economic relief and territorial pacification (it is important to remember that the 1383-1385 revolution gave priority to military architecture). The King ordered the built of Santa Maria da Vitória Monastery in Batalha, beginning probably in 1388, which is the date of a diploma where the King makes reference to a promise to the Virgin Mary to build a house of prayer for winning the Aljubarrota conflict against the Castilians (Pereira *et al.*, 2007).

So began the construction of the most important worksite of this period, to where converged great masters, not only Portuguese but also foreigners throughout the 15th and early 16th century. With the construction of this Monastery began the second cycle of the gothic architecture in Portugal, with the acceptance of the radiant style and introduction of the new decorative forms of the flamboyant style. These new decorative features were carried under the supervision of Master Huguet (1402-1438) and are visible throughout the façade of the church and at the main entrance. As examples of this decorative

repertoire are the characteristic tracery located on the upper part of the main window and the pinnacles decorated with floral motifs (Figure 2.1) (Dias, 1994).

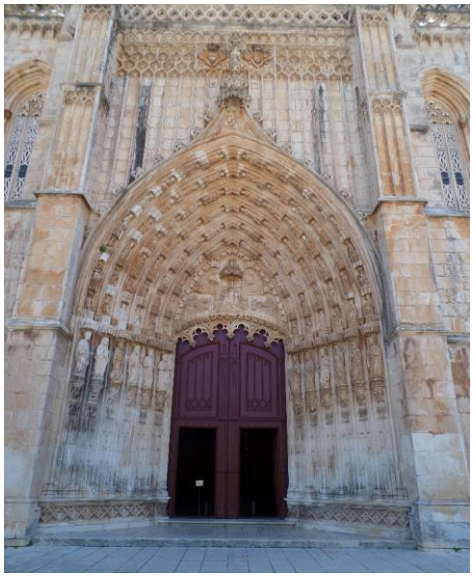


Figure 2.1 – Main entrance of Batalha Monastery. © Andreia Machado.

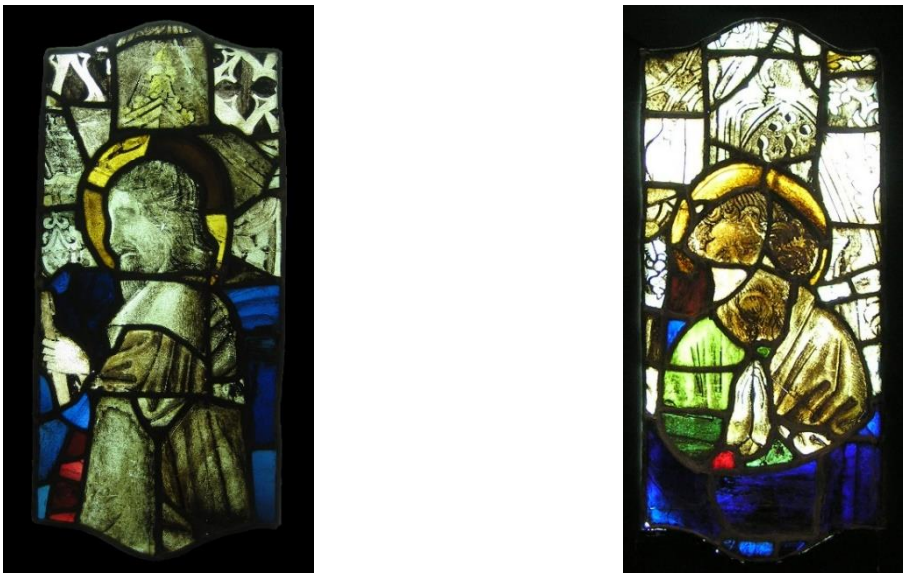
Since the construction of Batalha Monastery was under royal protection and funding, the adoption of new architectural and decorative solutions, such as stained glass, was to be expected. The oldest Portuguese stained-glass windows known until today belong to Batalha Monastery and are dated to between 1440 and 1480 (Redol, 2003). The work site of the Monastery became then the centre of stained-glass production in Portugal, where the majority of the glaziers and stained-glass painters established their work (Redol, 1995). The royal house becomes the main client during the 15th and 16th centuries, after which gradually loses its interest for this art form; the commissions decrease, leaving its professionals dedicated solely to the conservation of the existing windows. The last known royal commission is dated to 1582, which was performed at Batalha Monastery. Other commissions made during this period are known: Vila do Conde, Alcobaça, Sintra, Setúbal, Évora, Viana do Castelo and Tomar (Redol, 1995). It is only later in the 19th century that stained glass regains room on the Portuguese artistic panorama, not only with new creations but also with the preservation of the antique windows, namely the ones from Batalha.

2.1. The Monastery of Santa Maria da Vitória, Batalha – the beginning of a history

2.1.1. Stained-glass from 1440-1480

Figure 2.2 – Drawing from the longitudinal section of the church of Batalha Monastery by James Murphy.

As described in the previous section of this chapter, the oldest examples of Portuguese stained glass are located at Batalha Monastery and date to the 15th century. These panels were originally placed on the windows of the north and south lateral aisles of the church as also on the main windows (Figure 2.2) (Redol, 2003). The main theme depicted in the 15th-century group is the life of Christ, with the representations of the announcement to the pastors, the presentation in the Temple, the Baptism and Resurrection. Other figures are also portrayed: prophets, martyrs, and monks (Figure 2.3) (Redol, 2003). The study of both glass and glass paints of this assemblage was previously undertaken (Vilarigues and Da Silva, 2004; Vilarigues *et al.*, 2009, 2011). The stained-glass panels are composed of coloured and colourless glass pieces painted with grisaille. As for the type of glass employed, it is a potassium-rich glass with a high calcium content. The grisaille is the main painting technique applied. It is opaque, of brown and black colour with a heterogeneous morphology, with the presence of iron and copper grains embedded in a lead silicate matrix. The presence of zinc on the grisailles is also evident, attesting the use of a Cu-Zn alloy.



(a) (b)

Figure 2.3 – Two examples from the 15th-century stained-glass group from Batalha Monastery: (a) panel N14c *Prophet or Patriarch*, and (b) panel S07c, *Figure with a halo*. © Pedro Redol

2.1.2. Stained glass between the end of the 15th century and first half of the 16th century

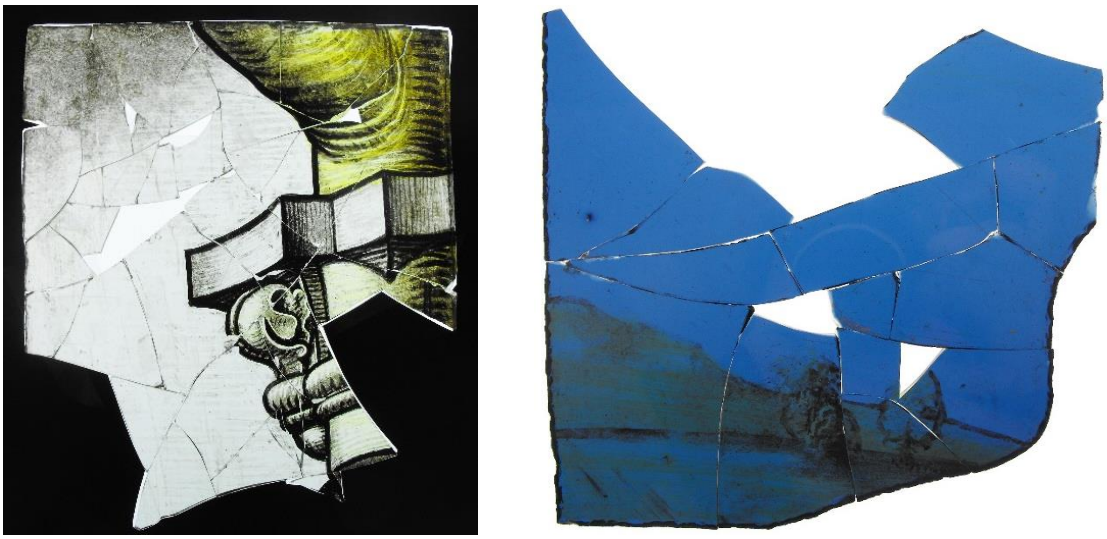
The group of stained-glass panels dated to between the end of the 15th century and the first half of the 16th century belongs to the lateral north and south aisles, where they were originally placed, and to the chancel, sacristy, and the chapter-hall, where the original stained-glass windows still remain. This ensemble presents a set of stained-glass panels with a more realistic composition and an attempt to humanizing the characters (Redol, 1995). They present without a doubt a higher quality technique when compared with the 15th-century group (cf. figures 2.3 and 2.4). The use of the grisaille painting is conjugated with the use of yellow silver staining. The type of glass employed is High Lime Low Alkali (HLLA) glass (Caen, 2009).

Figure 2.4 – Detail of the stained-glass panel *Flight into Egypt*, dated to the 16th century. © Andreia Machado.

As mentioned above, the art of stained glass in Portugal enters into decline in the end of the 16th century, with the last royal commission held at Batalha Monastery. In 1836, when King Ferdinand II travels to the north of the country and visits Batalha, he witnesses the advanced state of ruin of the Monastery. After his visit, a restoration campaign takes place, led by Luis da Silva Mousinho de Albuquerque (1792-1846). The original 15th and 16th century's stained-glass fragments which were found were reshaped into new figurative compositions, somehow incoherent, but at the time considered the best solution for the preservation of the existing fragments. The figures do not belong to the architectural and decorative arrangements on which are presented and even the figures itself are the product of the gathering of scattered fragments. As a result, there are currently 32 stained-glass panels of 70 cm x 35 cm. They were originally incorporated into timber frames, together with coloured glass pieces. They were removed from the windows and placed in storage in 1996. The second major intervention held at Batalha was in the 20th century led by Ricardo Leone (1879-1971) in 1931. The main plan was to preserve the stained-glass panels previously restored (Redol, 2003).

2.2. Charola from Convento de Cristo, Tomar – a recovered heritage

During two restoration campaigns carried in 1999 and 2009, a total of 423 loose stained-glass fragments, along with pieces of lead cames and seals, were found on the back wall of the wooden vault from the Saint Bernard chapel, located at the entrance of the Charola. The stained-glass fragments found were most likely from the windows' chapel. Joana Delgado performed the assemblage of the several fragments, a work carried during her master project entitled "Vitrais da Charola do Convento de Cristo em Tomar – História e Caracterização" (Stained glass from Charola of Convento de Cristo, Tomar – History and characterization) (Delgado, 2010). The criteria used for the assemblage were the union of the fragments, the colour and painting materials. The stained-glass groups that were assembled show a high-quality technique in terms of both the type of glass used and glass painting technique. From the several glass fragments, it was possible to recover a face, a Manuelin capital with what appears to be a wood trunk, two branches with a circular architectonic element and an acanthus leaf, which could also be part of a column. There is also a halo, which by its size does not belong to the face. These fragments are made of colourless glass painted with grisaille and yellow silver stain. Another group of stained-glass fragments was also recovered, composed of coloured blue glass painted with grisaille and yellow silver stain, and other group presents three shades of silver stain: pale yellow, strong yellow and orange (Figure 2.5).



(a) (b)

Figure 2.5 – Two sets from the 16th-century stained glass collection from the Charola of Convento de Cristo, in Tomar: (a) a Manuelin capital, and (b) a landscape. © Joana Delgado.

This assemblage is inserted into the iconographic program, of Manuelin influence, which dates possibly between 1510 and 1518 (Pereira, 1990). The same decorative style can be found in the Chapter Window and in the mural painting of the Charola. The yellow colour used to represent the trunks is transferred to the yellow silver stain used on the stained glass, for the same purpose (Figure 2.6). Another resemblance is the face, which reminds the figures that can be found inserted into the architectural elements.

This set presents a very detailed execution regarding the painting technique applied. In the case of the grisaille painting, applied to the face, the execution could be performed on several firing steps[8]: first, the grisaille was applied with a brush and then scratched to open areas for passing light. Then, another layer of grisaille was applied in order to shape the face, followed by a third application to define the contours of the face and shadows. The grisaille painting from this group presents a thin and opaque black grisaille, while the one from the 16th-century group from Batalha Monastery presents a thin and opaque brownish colour.

Regarding the application of the silver stain with various tones, from bright yellow to orange, reveals a very skilled technique which is not found in the stained-glass composition from Batalha Monastery (Delgado, 2010).

[8] The grisaille painting process of his set was assessed in the frame of a project undertaken by two master students from the Academy of Art and Design in Wroclaw, Poland. The students produced a replica of the face which is part of this set.

(a) (b)

Figure 2.6 – The resemblance between the iconographic program of the Charola and the stained glass is notorious, as we can see by the mural painting (a), represented on the stained-glass fragments, as seen in (b). © Joana Delgado.

As for the type of glass employed, it is a HLLA glass for the colourless, red and blue glass, and a potassium-rich glass with a high calcium content for the purple glass (Márcia Vilarigues, Delgado, & Redol, 2011). A first assessment was made on whether this glass was imported, as stated by a note of purchase dated to 1504 regarding a shipment of glass from Flanders (Redol, 2003). It is known that not only glass was exported from the Low Countries, but also stained-glass panels and technical expertise (Caen, 2009). The results obtained were compared with the results obtained for the glass used in the stained-glass panels of the coeval period from Batalha Monastery, as also from Flanders, Antwerp and Léon (due to its geographical proximity). As a conclusion, similar results were obtained only for the glass used for the stained-glass panels from Batalha Monastery, indicating a Portuguese glass production, which clearly evolved from the first stained glass panels from Batalha dated to the 15th century and this 16th-century group (Vilarigues et al. 2011).

2.3. The private collection of King Ferdinand II – a matter of taste

The private collection of King Ferdinand II (1816-1885), currently in exhibition at the Pena National Palace, is composed of stained-glass panels dated to between the 14th and the 19th centuries, with fine examples from Germany, Low Countries, and Switzerland. Collected and/or inherited by the King, the panels were placed in the dining room of the Palace of Necessidades in Lisbon, after which were stored in 1947 and transferred to Ajuda National Palace, where they remained until 1949. In the same year, they were transferred to Pena National Palace, where they were kept in storage (Martinho and Vilarigues, 2011; Rodrigues *et al.*, 2013). In 2011 the collection was presented for the first time to the public at Pena National Palace during the 16th triennial conference of the Committee for Conservation

of the International Council of Museums (ICOM-CC), at an exhibition entitled "Glass and Stained Glass – Ferdinand II's Passion", where it remains until today.

With the aim of shedding light on this unique collection, stained-glass panels *in situ*, as well as stained-glass fragments not incorporated in the exhibition are being studied in detail from historical and preservation perspectives. The set of German and Low Countries stained glass meets a group of heraldic panels, and panels about religious themes such as the representation of saints and the Virgin, and parables from the Bible (Figure 2.7). The panels present various sizes and were destined to be placed either in a religious or civil context.

(a) (b) (c)

Figure 2.7 – Three examples of the stained glass collection from Pena National Palace are presented here: (a) *Saint Gregory*, dated to the 16th century, Germany; (b) *Virgin of the Apocalypse*, dated to the 16th century, Germany and (c) *Flight into Egypt*, dated to the 17th century, Low Countries.

The set of Swiss stained-glass panels gathers a group of small-scale panels designed to be viewed up close, either in a religious or civil context. Their production reached its peak in the 16th and 17th centuries, when a great number of glass-painter's workshops were active in Switzerland but had faded by the 18th century. The panels usually show the coat of arms of the donor, and sometimes also his portrait; they depict religious themes or scenes of everyday life, such as representations of artisans at work. Illustrations of local history and legends are also frequent motifs (Hasler and Trümpler, 1998; Bergmann *et al.*, 2006). The early panels were usually made with traditional materials, using grisaille and silver stain as glass paints. From the second half of the 16th century onwards, the use of enamel paints became widespread (Figure 2.8).

(a) (b)

(c)

Figure 2.8 – The Pena National Palace collection presents a unique Swiss stained-glass group, with fine examples showing the quality of the several painting techniques: (a) Heraldic panel with the coat of arms of Niedersimmental, 17th century (PNP2860), (b) Heraldic Panel with the coat of arms of the canton of Luzern, 1688 (inscribed) (PNP2808) and (c) Heraldic panel *Ioannes Henricus Fleischlin*, 1688 (inscribed) (PNP2820).
© Luís Pavão, Parques de Sintra Monte da Lua S.A.

During the 18th century, when stained-glass windows fell out of fashion, many of the stained-glass panels were replaced by clear glass with few surviving in their original locations. Most of the dismantled panels were destroyed or sold on the flourishing art market between the end of the 18th century and the late 19th century, which is how many Swiss panels came to be in museums and private collections (Schneider, 1971; Giesicke and Ruoss, 2000).

CHAPTER 3

HISTORICAL TREATISES AND THE DISSEMINATION OF THE TECHNOLOGY

"Books of secrets have been with us from the beginning, standing in the shadow of the great ancient literature and chronicling the technical details of how we have shaped the world around us. They tell the tale not of where we sailed, but of how the ships were waterproofed; not of who amassed great fortunes, but the way the coins were minted; not of why a toast was raised, but of how to forge the goblets and distill the spirits."

Paul Engle (2014), "Conciatore, the life and times of 17th century glassmaker Antonio Neri"

For many scholars and philosophers of the Antiquity, glass was the clear evidence of the transmutation of materials; according to with Aristotle, it was possible to modify one body to another by means of the combination of the four elements: water, earth, fire, and air (Beretta, 2007). Pliny on his *Naturalis Historia* refers to the art of glass and its strict link with fire:

"Having now described all the creations of human ingenuity, reproductions, in fact, of Nature by the agency of art, it cannot but recur to us, with a feeling of admiration, that there is hardly any process which is not perfected through the intervention of fire. Submit to its action some sandy soil, and in one place it will yield glass, in another silver, in another minium, and in others, again, lead and its several varieties, pigments, and numerous medicaments. (…)
An element this, of immense, of boundless power, and, as to which, it is a matter of doubt whether it does not create even more than it destroys."

Pliny the Elder, "Naturalis Historia", book 36, chapter 68[9]

Glass is in its genesis the result of the fusion of the proper raw materials through the action of fire, a combination so different from the original materials that combined it, and to which is not possible to return to (Kerssenbrock-Krosigk, 2008). Glass was for this reason one of the materials most appreciated

[9] Pliny the Elder, *The Natural History*, book 36, chapter 68. (Friedrich and Mayhoff, 1855)(http://www.perseus.tufts.edu/hopper/text?doc=Perseus%3Atext%3A1999.02.0137%3Abook%3D36%3Achapter%3D68 – accessed on 4th October 2016).

by alchemists (Figure 3.1). In fact, alchemists took interest in many activities such as metallurgy, salts refinement such as potash or saltpeter, manufacture of pigments or the production of gems (Smith, 2008). Consequently, many glassmakers were also alchemists. Let us take the example of Antonio Neri, a glassmaker who worked at the *Casino di San Marco*[10] in Florence, and the author of *L'Arte Vetraria* (1612) (Beretta, 2014), Johann Kunckel, author of *Ars Vitraria Experimentalis* (1679) and the creator of the gold-ruby glass, or Johann Glauber, who took interest on the transmutation of metals, and achieved the process of the so-called Purple of Cassius, to which glass is coloured with a gold-tin solution.

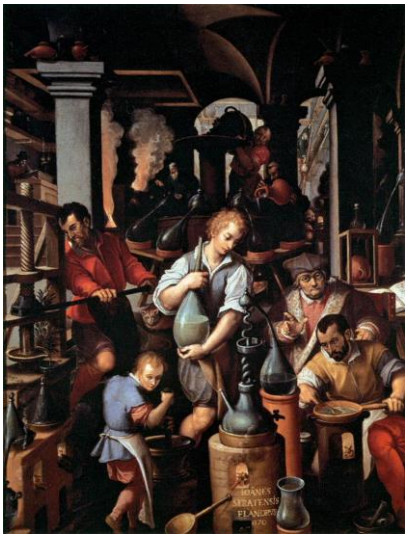


Figure 3.1 - *An Alchemist's Laboratory*, an oil painting by Johannes Stradanus from 1570, portraits the laboratory of Francesco I of Medici, located at the Palazzo Vecchio. This painting represents in detail the activity surrounding the *fonderie*, as we can also see the glass apparatus used by the alchemists. © Web Gallery of Art.

Many of the work carried by the alchemists is undocumented, being difficult to trace their research; they were very dependent on patrons, resulting in leaving unfinished projects once they deceased or lost interest on their experiments (Kerssenbrock-Krosigk, 2008). Many of this body of knowledge made its way to us today by the hands of many craftsmen and experts on glass and alchemy, through written texts that tell us the story behind this craft. One of the first written sources to mention the production of glass was found on Assyrian clay tablets dated to the 8th century BC. Pliny the Elder also mentions the art of glassmaking, including the raw materials used, where they were collected, and known working sites during that period, leaving out, surprisingly, the production in Egypt (Moretti and Hreglich, 2013).

The present chapter deals with the historical sources related to the procedures and materials used for the production of stained glass painting techniques and the production of stained glass. During the 19th century, the culture and spirit of the Romantic style arouse a great interest in this body of knowledge, particularly on the Medieval period. Many manuscripts were found, studied and translated to English

[10] The *Casino* was commissioned by Francesco I of Medici in 1574 to the architect Bernardo Buontalenti. The Prince was especially concerned with the reconfiguration of the laboratories placed at the *Casino*, the so-called *Fonderie* (Beretta, 2014).

and French, with a historical and artistic context of the art through the centuries. Mary Merrifield published in 1849 a ground-breaking work, the translation of several manuscripts on various arts, dated to between the 10th and the 17th centuries, including the manuscripts by Eraclius, Pierre Le Brun, and the Bolognese Manuscript. Earlier in 1844, Merrifield translated Cennini's *Il Libro dell'Arte* (Bugslag, 2008). The first translation to the work of Theophilus, *On divers arts*, was carried by G. E. Lessing and published in the late 18th century.

This revival of the Pre-Modern stained glass was also manifested on the flourishing art market of glass objects and stained glass from the 18th century until the end of the 19th century, with the purchase of many stained glass panels by private collectors or institutions. One example of this tendency is the private collection of King Ferdinand II located at Pena National Palace (described in chapter 2). The enthusiasm for this art was also transferred to the creation of stained-glass panels with the aim of portraying and copying the style and techniques of the Pre-modern (Figure 3.2).

Table 3.1 presents the list of several manuscripts and treatises from the Medieval period until the 19th century which were taken into account during this project.

(a) (b)

Figure 3.2 – The 19th century stained glass panel PNA38257 (a), from Ajuda National Palace, portraits a Swiss Knight, resembling the Swiss production of the Renaissance period, such as the stained glass panel PNP2860 (b), a Heraldic panel with the coat of arms of Niedersimmental, dated to the 17th century. © Luis Pavão, © Sara Martins.

3.1 The first sources

The first known manuscripts dealing with stained glass production is the well-known *De diversibus artibus*, written in the 12th century, between 1110 and 1140, by the Benedictine monk Theophilus, who has sometimes been identified as the German metalworker Roger of Helmarshausen, and to whom the creation of the portable alter of Paderborn is attributed (Hawthorne and Smith, 1979; Strobl, 1990). This work can be considered the first known technical treatise, with a well-defined structure, dealing with

painting, glass, and metalwork. There are known 7 manuscripts between the 12th and the 15th centuries, and several translations were published from the late 18th century onwards. The latest published translation is the work carried by Hawthorne and Smith, which is still today an important reference to better understand this treatise. There is also a Portuguese translation from 1984 edited by Virgolino Ferreira Jorge, with a brief note on the author of the treatise and a description of the translated publications available of *On Divers Arts* (which, curiously, does not mention the 1963 translation) (Jorge, 1984).

Theophilus presents himself as a humble servant, "unworthy of the name and profession of monk" (Hawthorne & Smith 1979, p. 11), offering with his manuscript the skills and expertise that he himself has received from God. In the prologue of book II we can attest the practice undertaken by Theophilus on the art of glass, as he mentions that "worked hard like a careful investigator using every means to learn (…) the variety of pigments could decorate the work without repelling the daylight and the rays of the sun" (Hawthorne & Smith 1979, p. 48). The second book, the one dedicated to glass and stained glass, comprises 31 recipes with mention to the various subjects regarding glass and glassmaking and stained glass production. The first three chapters indicate the construction of different types of furnaces for working glass, followed by a chapter about the raw materials to be used (with a specific indication to beech wood ash) and other regarding the preparation of the crucibles and their use to melt the glass frit. These chapters are followed by the ones on how to make coloured glass, glass sheets, flasks, and goblets. Then, Theophilus begins to explain how to prepare a stained-glass panel, by explaining how to prepare the wooden board to place the glass sheet, followed by the cut of the glass onto the desired fragments, and the preparation of the paint. Next, Theophilus demonstrates how to build a kiln for firing the painted glass fragments, and how these fragments should be fired. He finishes with the preparation of the lead cames, and with the assemblage of a stained-glass window. The information provided by Theophilus is up to date until today, being an important tool for understanding glass production in the Medieval period. Anyone who desires to prepare a stained-glass panel must have in mind the prescriptions that are given. Moreover, the use of beech ash for glassmaking is widely accepted within the archaeological and archaeometric studies (Freestone, 1992; Jackson and Smedley, 2008).

The second book ends with a chapter on how to repair a broken vessel and on how to make glass rings.

De diversibus artibus is the first technical treatise that makes mention to the art of glass and stained glass; nonetheless, previous works are worth mentioning. The Lucca manuscript *Compositiones and tingenda musiva*, also known as *Compositiones variae*, dates back to between the end of the 8th century and the beginning of the 9th century. This manuscript presents several recipes regarding many artistic techniques, among which we can find recipes about pigments and colouration of mosaic glass (Moretti and Hreglich, 2013; Neven, 2014). *Mappae Clavicula* is a compilation of older recipes of Greek origin, dated between the 4th and the 5th centuries. It was compiled around 800, with later additions dated to between the 11th and the 12th centuries. This manuscript includes more than 100 recipes present in the

Lucca manuscript. It presents recipes on how to make glass and how to paint on glass, a recipe for a white glaze, and how to cut glass (Smith and Hawthorne, 1974; Strobl, 1990; Neven, 2014). Other known compilation of older recipes is the manuscript attributed to Eraclius, *De coloribus et artibus romanorum*. This manuscript is dated to between the 10th and the 13th centuries. It contains recipes from *Mappae Clavicula* and Theophilus, and from Vitruvius and Isidore of Seville. It contains recipes on how to paint vases with grinded glass, glass engraving and making gems with Roman glass. We can also find several recipes for coloured glass, and for grisaille (Merrifield, 1849a; Moretti and Hreglich, 2013).

Dated to the end of the 14th century there is the treatise *Il Libro dell'Arte*, written by Cennino Cennini. It is a manuscript dedicated to the art of painting and the processes which are related. Henceforth, the part which is related to glass is from a perspective on how to paint on glass. Cennini in a way reports to the painter what he needs to make when approached by a glazier "with the measurements of his window, the width and the length" (Thompson 1954, p. 111). He also makes reference to the grisaille painting, brought by the glazier, "which he makes from well-ground copper fillings" (Thompson 1954, p. 111).
These manuscripts make references to the art of glassmaking and glass painting, however, we have to wait until the end of the 14th century to witness a treatise focused entirely on the art of stained glass. *Memoria del magisterio de fare fenestre de vetro* was written at the end of the 14th century by the glass painter Antonio da Pisa, who is believed to be the creator of one of the stained-glass windows from the aisle of *Santa Maria del Fiore* in Florence (Lautier and Sandron, 2008; Moretti and Hreglich, 2013). *Memoria* is a technical treatise with a strong practical writing: it is written as if it was a conversation between the author and the apprentice. This is also noticeable on the disorder with which the chapters are presented. Unlike Theophilus, who focuses mainly on how to make glass and to prepare the stained-glass window, Antonio da Pisa focuses on the glass painting: how to prepare the glass paint, how to paint the figures and backgrounds, and the firing of the painted glass fragments (with a chapter on how to build the kiln). His treatise presents recipes for grisaille, cold paint, and yellow silver staining, in fact, the first source to mention this technique (Boulanger, 2004; Lautier and Sandron, 2008). An important work around Antonio da Pisa and his *Memoria* is the one coordinated by Claudine Lautier and Dany Sandron (2008), who also presents an experimental exploration of this manuscript, testing many of the recipes, including the construction of the firing kiln.
There exists also a translation to Portuguese from 1989, in which the author presents this work in comparison with *On Divers Arts* manuscript (Jorge, 1989).
Following the work of Antonio da Pisa, but in a more concise manner, there is a manuscript from Sienna dated to the first half of the 15th century, attributed to Francesco Formica, the only known 15th-century glass painter from that region. It is inserted on a compilation of texts of several areas written during this period (Boulanger, 2004). The recipes regarding glass painting are more succinct when compared to the ones of Antonio da Pisa; on the other hand, the concern for the firing of the painted glass fragments is higher, with a detailed explanation of the various steps of the firing process accompanied by illustrations

of the kiln. Another treatise from the beginning of the 15th century is the one attributed to a monk from Zagan, which is inserted on a larger manuscript preserved at Wroclaw. It is believed to be based on the text of Theophilus, presenting recipes for grisaille and yellow silver staining, the firing of the fragments, how to make the lead cames, and how to place gems over the painted glass. From the second half of the 15th century, there is the *Kunstbuch*, preserved at Nuremberg. This manuscript is a compilation dedicated mainly to textiles. It contains only 6 recipes regarding stained glass, namely the preparation of a white grisaille and how to fire the painted fragments. It is followed by a brief description on how to make diamond-shaped fragments, to solder and assemble the stained glass window, and finally stained glass cleaning (Boulanger, 2004; Lautier and Sandron, 2008).

Published for the first time in the 19th century, there is knowledge of three Tuscan treatises dealing with glass techniques. They were compiled as a unique publication entitled *Dell'Arte del vetro per Musaico – tre tattatelli dei secoli XIV e XV ora per la prima volta pubblicati*. According to the author of this publication, the first two treatises can be dated between the end of the 14th century and the beginning of the 15th century and the third treatise is dated from 1443. The first and third treatises are anonymous, the second one was written by Benedetto Baldassare Ubriachi. The author mentions that Baldassare spent a considerable amount of time in Venice, therefore the recipes presented can be of Venetian origin (Milanesi, 1864). This compilation contains several recipes for colouring mosaic glass, glass for the imitation of precious stones, coloured enamels, *lattimo* and chalcedony glass, and coloured glass. On the second and third treatises, we can also find recipes for the preparation of *crocus martis* and calcination of tartar. On the third treatise, there is also a recipe concerning the purification of soda ashes (Milanesi, 1864; Moretti and Hreglich, 2013).

Also dated to the 15th century is known the *Segreti per colori*, an anonymous Bolognese manuscript. It is a compilation of recipes upon various arts, divided into eight chapters (Merrifield, 1849b). The seventh chapter comprises various recipes upon glassmaking, regarding colouring glass, and the production of enamels. It is followed by two other texts regarding the production of colours for mosaics.

The Montpellier manuscript (Ms. H. 486), of Venetian origin, is dated to 1536 and entitled *Recette per fare vetri colorati et smalti d'ogni sorte havute in Murano*. Presents various recipes on coloured glass, chalcedony and *lattimo* glass, coloured enamels and also the treatment of some of the raw materials used, like the calcination of lead and tin (Zecchin, 1987).

Dated to the 16th century is the *Marciana* manuscript, written in Tuscan dialect. Unlike the previous manuscripts of Italian origin, presents recipes to paint on stained glass, such as the grisaille and yellow silver staining, and also cold paint. There is a reference to the use of coloured enamels, however, prescribes the ones brought from Germany instead of giving a specific recipe (Merrifield, 1849b).

Written around 1560 is an anonymous manuscript of Venetian origin, found in 1982, and published in 2001 by Cesare Moretti and Tullio Toninato (Moretti and Toninato, 2001). Not only the influence of Murano is undeniable, as it is also believed that the author of this text, more than glassmaker was, in the

words of the editors, the bearer of the secrets behind this craft. This manuscript presents various recipes for the preparation of raw materials, several types of glass such as *lattimo* and chalcedony, the production of gems, mosaic glass, and enamels.

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Two important publications dated to the 16th century are the ones by Vanoccio Biringuccio and Georgius Agricola, two metallurgical treatises with mention to the art of glass, but more relevant, two important references on the state of the art of the metal technology during the Modern period. *De la Pirotechnia*, written by Biringuccio, was the first printed source concerning the metal arts and the work carried at the mines. It was published in 1540 shortly after his death, known to be before 1539. Referred to as "a neglected metallurgical classic", C. S. Smith makes the first introduction to Biringuccio's work (Smith, 1940), which would be later published in 1943 as a complete study of his treatise (Smith and Gnudi, 1943). Biringuccio was acquainted with the classic literature of Pliny and Aristotle, making brief references throughout the treatise, however, he was a man of experimentation, without too much concern for the theory behind the chemistry involved. His main source of information is his own observation and practice. Unlike Theophilus, who addressed this craft to the metalworker, Biringuccio was more concerned with the technology in which metallurgy was involved.

Regarding the information provided about glass, one must look to the fourteenth chapter of the second book. For Biringuccio, glass was a "fusible material that is almost made mineral by art and by the power and virtue of fire" (Smith & Gnudi 1943, p. 126). He was aware that Murano was the place where the glass was of higher quality. Biringuccio describes the process of making glass by adding two parts of quartz pebbles or river sand to one part of salt and adding the desired amount of manganese. The type salt to be obtained was not important to the process, though he recognises that using salt would give a better glass than adding simply the obtained ashes (Smith & Gnudi 1943, p. 132). He also makes special attention and description of the furnace and the pots to be used during the process.

His work was of major importance to the metal arts, but its impact was little when compared with the treatise *De Re Metallica*, written by Agricola and published in 1556, one year after his death. Agricola was the first scholar to recognize new metals after the seven known since the Antiquity, such as bismuth and antimony (Marshall and Marshall, 2005). He spent a considerable amount of time in the mines throughout the Saxony region. He observed the work which was carried out, discovered and named new minerals. The result of this work gave room to a complete treatise with a detailed description of the work around this activity. It is divided into twelve books, describing the mining process, the machinery involved, the role of the mining worker, the metals that can be found and the process of extraction and preparation (Agricola, 1950). The information about glass and glassmaking is presented in book twelve. Here, Agricola begins his discourse with the raw materials used for glassmaking. Like Biringuccio, he prescribes 1 part of quartz to two parts of salt, or plant ashes when the said salt is not available. He also prescribes the addition of *magnes*, which can be translated into manganese, in his words "to purify and transform green or yellow into white" (Agricola, 1950, p. 586). After the description of the raw

materials, Agricola makes a description of the furnaces to be used by the glassmakers, complemented by elaborate illustrations. This section is then finished with the way glassmakers work glass.

3.2. Spreading the word – Antonio Neri and the art of glass

3.2.1. Antonio Neri – the man and the treatise

Antonio Lodovico Neri (1576-1614) is a character to whom glassmakers and glass researchers are today in great debt. He was a priest, an alchemist and above all an enthusiast of glass and glassmaking. Luigi Zecchin was the first to uncover the baptism records of Neri, opening the way to the reconstruction of the genealogical tree of the Neri family. We can see this work fully described in the publication by Paul Engle, *Conciatore* (2014).

From an early age, Neri gains contact with the alchemical arts. It is most likely that as a child he visited the *Casino di San Marco* with his father. Between 1598 and 1600, Neri writes a manuscript called *Il Tesoro del Mondo*, which is a compilation of various illustration of glass, furnaces, chemical instruments, and mining. At this point, Neri was most likely working at the *Casino* performing experimentations on glassmaking and preparation of the raw materials. Many of these experiments are documented on a set of 27 letters dated to between 1601 and 1611, preserved at the Biblioteca Nazionale Centrale di Firenze (BNCF Ms. II. I. 391), which document the correspondence between Antonio Neri and Emanuel Ximenes, a Portuguese merchant-banker and citizen of Antwerp (Boer and Engle, 2010). This friendship allowed Neri to travel to Antwerp to develop new glasses and other recipes on the alchemical arts. There is knowledge of him working in Pisa in 1602, for a letter to Ximenes regarding the production of enamels. He returned to Florence in 1611 and delivers the manuscript *L'Arte Vetraria* to be published in 1612, which is a compilation of the work carried in Florence, Pisa, and Antwerp. *L'Arte Vetraria* is the first published systematic treatise on glass and glassmaking (Figure 3.3).

The Venetian influence in *L'Arte Vetraria* is notable, whether he had direct contact with the Venetian anonymous manuscript (above cited), or by the Venetian glassmakers present in Florence working at the *Casino* (Moretti and Toninato, 2001; Beretta, 2014). *L'Arte Vetraria* is a work that Neri dedicates to "the honourable gentleman Don Antonio Medici", to whom he refers as his "outstanding patron", placing in evidence Neris' close connection with the *Casino* (Engle 2003, vol. I, p. 2). We can see some resemblances between the prefaces of Neri and Biringuccio, especially in the beginning of his discourse, when he states that "glass is a true fruit of the art of fire, as it can so closely resemble all kinds of rocks and minerals, yet it is a compound, and made by art". He praises the importance of glass to the use and benefit of many, referring its use for the production of several kinds of purposes (Engle 2003, vol. I, p. 4). The treatise is divided into seven books. The first chapters of his treatise deal with the preparation of raw materials, followed by the preparation of various types of glass – lead glass, chalcedony, *lattimo*.

On the sixth book, Neri presents the recipes for enamels of colours. This treatise reveals that Neri does not base his work only in theoretical and practical experiences of others, but also in his own experience, testing and verifying each step of the glassmaking process (Engle 2003, vol. I, p. 2).


L'ARTE
VETRARIA
DISTINTA IN LIBRI SETTE
DEL
R. P. ANTONIO NERI
FIORENTINO.
Ne quali si scoprono, effetti marauigliosi, & s'insegnano segreti bellissimi,
DEL VETRO NEL FVOCO
& altre cose curiose.
ALL'ILLVST.mo ET ECCELL.mo SIG.
IL SIG. DON ANTONIO MED.CI.
IN FIRENZE.
Nella Stamperia de' Giunti. M. DCXII.
Con licenza de' Superiori.

Figure 3.3 – *L'Arte Vetraria, distinta in libri sette.*

3.2.2. Beyond *L'Arte Vetraria* – the translations

Neris' publication gained a new momentum thru Christopher Merrett, one of the fellow founders of the Royal Society in 1660. Written in 1662, *The Art of Glass* was the first translation of Neris' *L'Arte Vetraria* and the first English publication regarding glassmaking. Merrett was back in his time dedicated to many fields of interests: in addition to being a fellow of the Royal Society, he was a renowned physician, botanist, and a librarian. He was the responsible for preparing a detailed catalog of the Royal Society library in 1660 (Turner, 1963). Being an active member of the Society and fully dedicated to many areas of expertise, it is not surprising that he was appointed to be the translator of Neris' work. In addition to translating the treatise, Merrett comments many of the chapters with additional information that he thinks is relevant to the reader. To whom he refers as the "ingenuous reader", Merrett informs that many of the repeated information that appears in the original manuscript is omitted, giving a brief account of these repetitions before the translation of the treatise (Merrett 1662, p. XXI). In addition, there seems to be some lack of knowledge when discussing some matters, for example regarding the preparation of zaffer[11] in chapter 12. Merrett does not know its origin, only acknowledging it must be some invention from Germany, a mixture of brass, sand, and *lapis calaminaris* (meaning zinc carbonate). Not only does Merrett suggests that brass is the responsible for the blue colour but also states that the experienced Agricola does not mention its existence in his treatise (Merrett 1662, p. 279), which is not true, since Agricola makes reference to zaffer, however referring to it as *cadmia metallica*. If some information is presented incorrectly, on other cases Merrett goes beyond and does an extensive approach, as is the case of the comments made related to the use of the several types of ashes to make glass.

Despite some incoherencies and lack of knowledge regarding some raw materials used, Merrett was indeed the first to make an extensive account of the glassmaking process in the seventeenth-century England. To better serve this task, he sought Italian glassmakers who remained in England during this period for a better understanding of the raw materials and processes used by Neri (Mauck, 2012). His

[11] Zaffer is the product obtained from the calcination of a cobalt ore. It was used for the production of blue pigment, to be used on glass, enamels, glazes, and painting. A detailed explanation can be found in chapter 4, pp. 50-51.

translation of *L'Arte Vetraria* opened the way to several translations, corrections, and annotations throughout Europe.

An important contribution dated to the end of the 17th century is the one by André Félibien, *Des Principes de l'Architecture, de la Sculpture, de la Peinture, et des autres arts qui en dépendent*, written in 1676 (Félibien, 1697). This is a general treatise dealing with the three main art forms from that period: architecture, sculpture, and painting. Félibien was, according to the description present in the cover of the treatise, the secretary of the Academy of Sciences as also a historiagrapher of the Kings' buildings. It is therefore not surprising that the first book, concerning architecture, is the most extensive one. Chapter 21 of this book is concerning glass, most specifically stained glass. Here the author explains briefly how to assemble a stained glass panel, how coloured glass painted with grisaille was used to present figurative compositions during the Gothic period, and its development to the use of colourless painted glass. For glass painting, Félibien describes the grisaile, sanguine and enamel painting techniques and the way to apply them on glass. In addition, he describes the firing process for the painted glass fragments. Besides of this chapter concerning glass and glass painting, Félibien revisits this issue in book three, concerning the art of painting. Chapter IX is concerning cold painting on glass, and reverse glass painting. From the many authors that Félibien recalls regarding the art of glassmaking and glass painting, Antonio Neri is not one of them.

Contemporary to the work of Félibien, an important treatise and a reference to the art of glass, is the one by Johann Kunckel, *Ars Vitraria Experimentalis, oder Volkommene Glasmacherkunst*, written in 1679. Johann Kunckel was an alchemist (and the son of an alchemist) and in 1678 was in charge of the Potsdam glass factory sponsored by the "Great Elector" Prince Friedrich Wilhelm of Brandenberg (Hunt, 1976). Kunckel's treatise was later translated into French in 1752 by Paul Thiry d'Holbach.

He compiled into one single work the translation of Neris' *L'Arte Vetraria*, adding the comments made by Christopher Merrett in 1662, his own comments to Neris' work, and also his own experiments in glassmaking. Besides Neris' treatise, Kunckel presents 100 recipes, verified by "practice and experience" (Holbach 1752, p. 327), and divided into three books: the first includes recipes on glassmaking, colouring glass, and gilding on glass; the second book comprises recipes on enamels and glazes; the third book includes various recipes on how to prepare varnishes, and other "useful" recipes concerning glass painting. An important account of Kunckel's contribution is the comments made to many of the chapters of Neri's treatise. As an example, is the comment made to chapter 12, regarding the preparation of zaffer, where the author explains that the one described by Neri is not necessary; he then makes a detailed description of the place of extraction of the cobalt mineral, the preparation and trade of this material. At the end of the first part of his treatise, Kunckel presents his remarks on the preparation of salt from plant ashes, and of potash (Holbach, 1752).

Another treatise important to consider is the one by Robert Dossie, *The Handmaid to the Arts*, written in 1758. When entered in the Society or the Encouragement of the Arts, Manufactures and Commerce in 1760, Robert Dossie had a significant reputation as a practical chemist in Europe. He was the son of an apothecary with an extensive knowledge of pharmacy, industrial arts, and chemical manufactures. This treatise can be considered as an important compilation of many industrial arts. Along with this publication, the author gave other contributions, such as the one regarding the production of potash (Gibbs, 1951). The publication starts by representing its purpose, to teach "the nature, use, preparation, and composition, of all the various substances employed in painting", including "those peculiar to enamel and painting on glass", among other arts. The preface, extensive and informative, explains the importance of the publication to the arts in Great Britain, as cited above, to surpass France, which at the time "have got greatly the start of us in this very material pursuit" (Dossie 1758, p. vi). Regarding the art of glass, Dossie is familiar with previous works in the field. He discusses in the preface the work of Antonio Neri, considering it the "foundation for all the collections of recipes of that kind", and the translation undertaken by Christopher Merret, which allowed the dissemination of Neri's publication. Also referenced in the preface is the translation of Neri's work to German, performed by Kunckel (Dossie 1758, p. xviii). Concerning painting on glass, Dossie focuses on enamel paint. Enamel recipes presented in his treatise are original and might have been experimented by the author or by others, on whose work and expertise he relied on (Dossie 1758, p. 24).

Other 18th-century important treatise is the one by Pierre Le Vieil, *L'Art de la Peinture sur Verre et de Vitrerie*, from 1774. Le Vieil was a French glazier master with an extensive knowledge on glassmaking and an enthusiast looking forward to rediscovering the old techniques forgotten during the 18th century (Brisac, 1989). In the preface of the manuscript, Le Vieil begins by sharing his concern on the importance of both research and promotion of the knowledge of the Arts to the posterity. Then, the author makes a reference to the art of glass of the Antiquity and a brief account on the state of the art between the 12th and the 16th centuries, which he elaborates on the first chapters of the first part of the treatise. This work is divided into two parts, as explained by the author: the first part of the treatise is dedicated to the history of glass painting over time, the artists behind this craft, and its decay. In the second part, Le Vieil presents the technical aspects of this craft, presenting the several recipes of ´grisaille, yellow silver staining, enamels, and sanguine red. It is considered an important publication regarding the production of glass, presenting original family recipes and the translations from Antonio Neri, Kunckel, and "an Englishman", to be known Robert Dossie (Vieil, 1774).

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In the 19th century, the glass production takes a new direction towards the industrialization of the glassmaking process. An example is the substitution of the use of conventional raw materials, such as plant ashes, for new industrial-making processes like the Leblanc process, used for the production of synthetic soda (Moretti and Hreglich, 2013).

The documentation provided during this period also adapts, with the publication of complete works concerning glass production, dealing with every aspect of it. In addition, a historical introduction of the glass and stained-glass panorama through the centuries is presented, with a comparison with the current reality (of that period).

First published in 1825 is the treatise *Nouveau Manuel Complet de la peinture sur verre, sur porcelaine & sur émail, des émaillages industriels et de la fabrication des émaux et des couleurs vitrifiables*, written by Reboulleau et Magnier. As said above, begins with a historical consideration about the stained glass art through the ages, with the transcription of other publications in the field. It is divided into 4 parts: the first considers the glass painting, the second regards painting, gilding and silvering of porcelain, the third part enamelling, and finally the fourth part general notions regarding the previous chapters in an attempt to connect the over-all knowledge, "contained therein to all parties, without applying exclusive more to one than to another" (Reboulleau and Magnier, 1866).

Georges Bontemps wrote the *Guide du Verrier*, first published in 1868. This is a complete treatise on the glass production, glass technology, and painting. Bontemps begins to emphasize that this work is a culmination of forty years of experience in glassmaking. Like the previous publication, this work begins with a historical introduction on the stained-glass panorama through the ages, followed by the exposition of every aspect involved, chapter by chapter. On the second book, Bontemps recollects the sales prices of glass, from the 18th century to his present time (Bontemps, 1868).

Table 3.1 – Treatises regarding glass production, glass painting and enamel painting, from 12th to 19th centuries.

Title	Author	Period	Origin	Notes
De Diversibus Artibus	Theophilus	12th cent. (c. 1100)	Germany	Divided in 3 books. The second book regards the production of stained glass, and painting on glass (grisaille).
Liber diversarum arcium	Anonymous	14th cent. (c. 1300)	North of Europe	Compilation of c. 580 recipes, comprising several painting techniques, including glass painting and painting on ceramics.
Secreti per lavorar li vetri secondo la dottrina de M.ro Antonio da Pisa	Antonio da Pisa	14th cent.	Italy	Stained glass production, emphasizing glass painting, namely silver staining.
Dell'Arte del vetro per Musaico – tre tattatelli dei secoli XIV e XV	Anonymous; Benedetto Baldassare	14th and 15th cent.	Tuscany	Compilation of 3 treatises, the first two anonymous, the third by Benedetto Baldassare, regarding the production of enamels and coloured glass. The third treatise present probably the first recipe about chalcedony glass.
Segreti per colori	Anonymous	16th cent.	Bologna	Presents a chapter regarding glass for imitation of precious stones and enamels.
Antwerp Manuscript	Anonymous	16th cent.	Antwerp (?)	3 recipes on enamel production (blue, purple and green)
Recette per fare vetri colorati et smalti d'ogni sorte havute in Murano	Anonymous	16th cent. (1536)	Italy	The Montpellier manuscript. Presents recipes about coloured glass, chalcedony glass and enamels.
De la Pirotechnia	Vanoccio Biringuccio	16th cent. (1540)	Italy	Treatise concerning several minerals, their origin and mining process. Presents a chapter concerning glass (chapter 14).
De re metallica	Georgius Agricola	16th cent. (1556)	Germany	Treatise about mineralogy. Chapter 12 deals with the production of glass, with special attention to furnaces.
Ricettario anonimo del'500	Anonymous	16th cent. (c.1560)	Italy	Recipes concerning raw materials for glass production, coloured glass, lead glass, glass for imitating precious stones, mosaic and enamels.
L'Arte Vetraria	Antonio Neri	17th cent. (1612)	Florence	Complete treatise on raw materials for glassmaking, preparation and colouration of lead glass, imitation of precious and semi-precious stones, coloured glasses, chalcedony glass, gold ruby glass and enamels of various colours.
Copie de tutti li secreti de smali cavate dalli libri et alter carte della buona memoria di mio padre…	Giovanni Darduin	17th cent. (1644)	Murano	Descendant of an important Venetian glassmaker family. Compilation of recipes from his father Nicolò.

Table 3.1 – (Continue)				
Libro de'segreti cavato da molti mastri di cristali et da altri homeni literati…	Gasparo Brunoro	17th cent. (1645)	Gdansk	Divided in two parts, only the first concerns glass production. It compiles several sources, such as the treatises by Neri, Darduin, the Montpellier manuscript and the anonymous manuscript from 16th century.
Recueuil des Essaies des Merveilles de La Peinture (Brussels Manuscript)	Pierre Le Brun	17th cent. (1635)	Paris	Chapter 4, explaining the process on how to paint on glass, with references to grisaille painting and silver staining.
The Art of Glass	Christopher Merrett	17th cent. (1662)	London	First translation of the work by Antonio Neri, important for its dissemination throughout Europe.
Des Principe de L'Architecture, de la Sculpture, de la Peinture	André Felibien	17th cent. (1676)	Paris	Chapter 21 of the first book refers the method to paint on glass, and enamel production.
Ars Vitraria Experimentalis	Johann Kunckel	17th cent. (1679)	Leipzig	
De l'Art de la verrerie	Haudicquer de Blancourt	17th cent. (1697)	Paris	Many similarities with the work by Félibien, possibly a copy without reference to the source.
L'Art de la Verrerie	Baron d'Holbach	18th cent. (1752)	Paris	Compilation of his translation of Arte Vetraria and both translations of Merret and Kunckel
The Handmaid to the Arts	Robert Dossie	Séc. XVIII (1758)	London	Presents several recipes of enamel paining, both base glasses and the various colours.
L'Art de la peinture sur verre et de vitrerie	Pierre Le Vieil	18th cent. (1774)	Paris	Divided into 2 parts. The second part presents the several aspects os glassmaking and enamel painting, with references to Antonio Neri and Robert Dossie.
Nouveau Manuel complet de la peinture sur verre sur porcelaine et sur émail	Reboulleau et Magnier	19th cent. (1883)	Paris	Divided in 3 parts, the first regards glass painting. Evidence to stained glass painting.

CHAPTER 4

PAINTING TECHNIQUES APPLIED ON STAINED GLASS: THE REPRODUCTIONS

4.1. Blue Enamel[12]

The use of enamels in stained glass began to appear in the second half of the 15th century (Caen, 2009). The introduction of enamels in stained glass was an innovation at the time, allowing an increase of the colour range to use into one single glass piece. The complete colour palette was progressively introduced during the next fifty years: first the colour blue, followed by purple, brown, carnation red and last green (Cannon, 1991). The first known written evidence (until today) of enamel recipes is a treatise from the 16th century, *Die maniere van ovens te maken om colueren te backen van alle soerten*, known as the Antwerp Manuscript from the Plantin-Moretus museum collection (M. 64). Enamel recipes became widespread through the work of Antonio Neri, *L'Arte Vetraria*, published in 1612. His recipes can be re-visited in the works of Merret (1662), Kunckel (1679) and Le Vieil (1774) (Table 4.1).

For the reproduction and characterization of blue enamel painting, two treatises were approached: the 17th-century treatise *L'Arte Vetraria* written by Antonio Neri, and the 18th-century treatise *The Handmaid to the Arts*, by Robert Dossie. The study and characterization of selected raw materials used for blue enamel painting was performed, namely quartz pebbles, plant and wine lees' ashes, and a cobalt ore, skutterudite. The aim was to chemically characterize the raw materials individually, and to evaluate their influence to the final paint. Moreover, the reproduction of selected enamel recipes was conducted, followed by corrosion tests of both enamel powder and paint samples. They were chemical and morphologically characterised by means of a multi-analytical approach. The description of the different analytical techniques is presented in Appendix I.

[12] The contents of this subchapter are published in: Vilarigues, M. and Machado, A. (2015) 'Pintar com luz: o esmalte azul na pintura de vitral', *Química*, 137, pp. 31–35; Machado, A. and Vilarigues, M. (2016) 'Cobalt blue - reproduction and characterisation of blue enamel recipes from The Handmaid to the Arts by Robert Dossie', *Glass Technology: European Journal of Glass Science and Technology Part A*, 57(4), pp. 131–140. DOI: 10.13036/17533546.57.4.027.

4.1.1. The recipes

***L'Arte Vetraria* (1612): raw materials and recipes**

The production of blue enamels described in many recipes from historical treatises from the 17th and 18th centuries are anchored in the work of Antonio Neri. The sixth book of the treatise presents the production of enamels into two steps: first, the production of a base glass (chapter 93, *Materia con la quale si fanno tutti li Smalti*) and secondly the production of each individual colour. For the blue enamels, Neri proposes three recipes: two for turquoise enamel (chapter 95, *Smalto turchino*) and other referred to "other blue enamel" (chapter 96, *Altro Smalto azurro*), the enamel recipe which was reproduced in this study:

93. The Material to Make all Enamels

Take for example 30 lbs of fine lead, and 33 lbs of fine tin. Blend these metals together and calcine them in the kiln, as was described for lead in its place (…)

Take 50 lbs of this fine calx, and 50 lbs of crystal frit made with thoroughly ground white tarso. Through a sieve, sift 8 oz of white tartar salt (…) set this material down in the terracotta pot again, giving it fire for 10 hours.

Remove the material, pulverize it well, and store it in a dry place. (…)

96. Another Blue Enamel

As an example, take 4 lbs of enamel base material. With this, thoroughly mix 2 oz of prepared zaffer, but first mix in 2 pwt of thrice cooked copper, made with the flakes of the kettle smiths, as was described in its place. (…) When it is fused and well clarified, dump it into water, and repeat. (…)

Paul Engle (2003), "L'Arte Vetraria/The Art of Glass", vol. III, pp. 22 and 26

Table 4.2 presents the raw materials indicated by Antonio Neri and their current chemical formula.

Table 4.2 – Raw materials and related chemical formula of the components used for the production of blue enamels according to the recipe *Altro Smalto Azurro* by Antonio Neri.

Base glass	*Cristallo frit*	*Tarso* (Pebles from Ticino river)	SiO_2
		Polverino salt (salt from coastal plant ashes)	Na_2CO_3
		Sal di Tártaro (salt from ashes of wine lees)	K_2CO_3
		Lead and tin calx	Pb_2SnO_4
Blue enamel		*Zaffera*	CoO
		Ramina di tre cotte (calcined copper)	CuO

Table 4.1 – List of the blue enamel recipes from historic treatises dated to between the 17th and the 18th centuries.

		Zaffer	Smalt	Blue enamel	Copper	*Cristallo* frit[13]	White glass / Venetian glass / Flint glass	Coloured blue glass[14]	Lead glass	Quartz pebbles	Sand	Salt / common salt / sea salt	Soda	Rock salt (*sel gemme)*[15]	Lead and tin calx	Lead ashes / Litharge / *mine de plomb*	Tartar salt / Pearl-ashes[16]	Calcined tartar	Saltpetre	Borax	Arsenic	Mercure	Bismuth
L'Arte Vetraria (1612) Antonio Neri		X			X	X									X		X						
Libro de'segreti…(1645) Gasparo Brunoro	1	X			X	X									X		X						
	2	X			X	X																	
Des Principe de L'Architecture, de la Sculpture, de la Peinture (1676) André Félibien		X									X					X							
De l'Art de la verrerie (1697) Haudicquer de Blancourt		X									X					X							
Ars Vitraria Experimentalis (1679) Johannes Kunckel	1[17]	X					X			X		X				X		X					
	2	X								X						X		X					
	3	X					X			X		X			X			X					
	4	X								X		X				X		X					
	5[18]	X									X					X							
	6	X								X						X							
	7	X								X						X							
	8	X					X			X						X		X					
The Handmaid to the Arts (1758) Robert Dossie	1	X							X			X					X						
	2	X							X								X			X	X		
	3	X							X			X					X						
	4	X							X								X			X	X		
	5	X					X					X					X			X				
	6	X					X					X					X			X	X		
	7	X					X					X					X			X				
	8	X					X					X					X			X	X		
L'Art de la peinture sur verre et de vitrerie (1774) Pierre Le Vieil	1			X									X										
	2			X										X				X	X				
	3	X					X											X	X			X	X
	4		X													X		X					
	5			X				X															
	6			X				X										X	X				
	7			X				X										X					

[13] *Cristallo* is a sodium-rich glass, that appeared in Murano in the 15th-century. It is considered a glass of high quality, known by its transparency. It was made from salto f Levantine ashes and quartz pebbles from the Ticino river.
[14] There are three recipes on the manuscript by Pierre Le Vieil (p. 118) which present the terms *aigue-marine* (aquamarine) and *azur de mer*. The author states that these components might not have been related with the employment of precious stones (take the example of *aigue marine*, which is a term for beryl, a beryllium and aluminium silicate), rather related with the employment of glass or gems with this colour. The author then mentions recipes given by Antonio Neri, on how to give glass an aquamarine colour.
[15] Rock salt, or *sel gemme*, is the mineral form of sodium chloride (NaCl) that we can find in nature, known as halite.
[16] Potassium carbonate, K_2CO_3.
[17] The recipes given by Kunckel have the employment of salt. The author does not mention which type of salt is employed, however we can assume that it is a common salt, such as sodium chloride, since in previous recipes the author mentions the word *potasse*, potash, meaning the salt from terrestrial plant ashes.
[18] For this recipe the author mentions the employment of zaffer, or in the lack of this component, the use of a blue enamel, which might be any recipe given the author, or the recipe given by Neri.

Neri makes reference to the use of *Tarso*, "a specie of very white marble" (Engle 2003, vol. I, p. 15), an inaccurate word used for quartz, collected on the shores of the Ticino river, and in Tuscany, at Mount Veruca in Pisa, Sevarezza, Massa and in the Arno river. The author also states that these pebbles must be free of dark veins and, that for crushing and milling stone mortars have to be used instead of mortars made from bronze or another type of metals in order to prevent any type of contamination of the milled pebbles. The use of pebbles in glass production is already mentioned in previous treatises, such as the Montpellier Manuscript, dated to 1536 (Zecchin, 1964). The Ticino pebbles chosen by Neri for the production of the *Cristallo frit* are very rich in silica, without "dark veins, or the yellowish appearance of rust" (Engle 2003, vol. I, p. 15).

Samples from the pebbles of Ticino River[19] were analysed by ICP-MS (Table 4.3). These results attest the high level of purity of this raw material, with a very high concentration of silica and low concentration of alumina, iron and titanium, when compared with the chemical composition obtained from sand sources previously analysed (Turner, 1956; Brems *et al.*, 2012).

Table 4.3 – ICP-MS analysis of the Ticino pebbles (wt. %).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MnO	TiO_2
99.9	0.03	0.02	0.04	0.003	0.003

The coastal plant ashes for the production of *polverino* salt came from the Levant region, currently Syria, and were considered by Neri the best when compared to the Spanish soda. In his treatise, he describes the preparation and purification of these ashes in order to obtain the salt which would be mixed with the finely ground *tarso*. Antonio Neri refers to this type of imported ashes as *Rochetta*, the bulk material, or as *Polverino*, the obtained powder (Engle 2003, vol. I, p. 11). In the 17th century, there is a reference to the use of *Barrilla*, sodic ashes imported from Alicante, Spain. Moretti (2013) mentions that for a short period of time *Barrilla* was also produced from local plants from Lido, along the Venetian coast and at the Po River (Moretti & Hreglich 2013, p. 30). From the 15th century onwards, potassium-rich ashes were used, obtained from plants such as fern (Engle, 2003; Moretti and Hreglich, 2013). Neri also mentions the use of salt fern ashes, as is described in chapter 5 of the first book (Engle 2003, vol. I, p. 20).

Several studies were performed in order to assess the composition of the different types of plant ash. They can present a variable chemical composition between plant and wood ash (Stern and Gerber, 2004, 2009; Jackson, Booth and Smedley, 2005), and between the ashes from the same species collected on neighbouring sites (Sanderson and Hunter, 1981), or the type of substratum on which they grow (Stern and Gerber, 2004). Also important is the variability that can be found in different parts of the same plant (Smedley, Jackson and Booth, 1998). Another aspect that can contribute to the variability of the

[19] The samples were kindly provided by Professor Maria Pia Riccardi, from the Earth Science and Environment department from the University of Pavia.

chemical composition is the ashing temperature: Misra *et al.*(1993) verified for wood ash that a dissociation of potassium and calcium carbonates between 700 ºC and 900 ºC (depending on the wood type), with the volatilization of potassium between 800 ºC and 900 ºC. Regarding calcium, its content increases due to the dissociation of the above-mentioned carbonates and the volatilization of the potassium oxide formed after the dissociation.

The use of untreated ash, especially wood ash, can introduce contaminants on the final glass, such as iron, resulting in an undesirable green hue. The use of plant ash was therefore in many cases preferable, leading to various solutions (Rehren and Freestone, 2015).

As for the glassmakers in Central Europe, limestone was added to the batch in order to get a clearer (and more stable) high-quality final product (Rehren and Freestone, 2015). Another solution was the treatment of the ashes, which consisted on the lixiviation of the insoluble compounds of the ash, remaining a salt rich in potassium carbonate, potash. However, previous studies concerning the production of glass have revealed that the 2-component glass batch (sand:ash) using whole-ash would be the most common practice (Stern and Gerber, 2009), and that the glass production using potash would occur only in certain regions, as we can attest by the study on Bohemian glass conducted by Cílová & Woitsch (2012).

For the present study, fern plants[20] were collected and dried for 10 weeks and burned in order to obtain the ashes to be analysed. They were fired on a turned over terracotta vase, this way restricting the entrance of oxygen. The ashes were ground in a stone mortar and sieved, repeating this process twice. A sample of these ashes was re-ashed at 850ºC on an electric furnace in order to remove the remaining carbon (Jackson, Booth and Smedley, 2005). The final ash was of white-grey appearance. The results obtained (Figure 4.1) gave a very inhomogeneous composition, an expected result obtained for terrestrial plant ashes, as attested by previous works. The main components identified were potassium chloride, sodium calcium silicate, and potassium sodium calcium phosphate. These compounds are soluble in silicate melts, with exception of sodium and potassium chlorate (which is partially soluble), which will have an impact on the final composition of the glass (Jackson, Booth and Smedley, 2005). On the first half of the 15th century, a new method of purification of the ashes was introduced, in order to obtain a salt, rich in sodium or potassium carbonate (Moretti and Hreglich, 2013). The lixiviation of the ashes is mentioned in the Montpellier Manuscript (1536), and also on the Biringuccio's *De la Pirotechnia* (1540), where the author states that this salt is usually called potash (Smith & Gnudi 1943, p.112). Neri explains that to extract the salt from fern ashes is to be made with "the rules, observations, and diligence prescribed for Levantine *polverino* salt…" (Engle 2003, vol. I, p. 20): the ashes are boiled, forming an alkaline concentrated solution called lye. The ashes are mixed continuously until half of the amount of water evaporates. After this process, the solution rests for about two days after which the procedure is repeated again until the solution becomes whiter. In the end, the lye is placed on a low fire. After 24

[20] Ferns were collected from a private property, near Tomar.

hours, a white salt, “that looks like spider webs or white lace” (Engle 2003, vol. I, p. 13) appears in the walls of the container, and that product is the salt rich in potassium carbonate. The lixiviation of the fern ashes, as instructed by Neri, gave a browner salt, as the ashes obtained were completely black (Neri does not mention the colour of the ashes imported, or if there was any difference, between maritime and terrestrial plant ashes. Another hypothesis is the burning process). µ-EDXRF analysis to the obtained salt revealed the presence of potassium, calcium and chlorine (Figure 4.2).

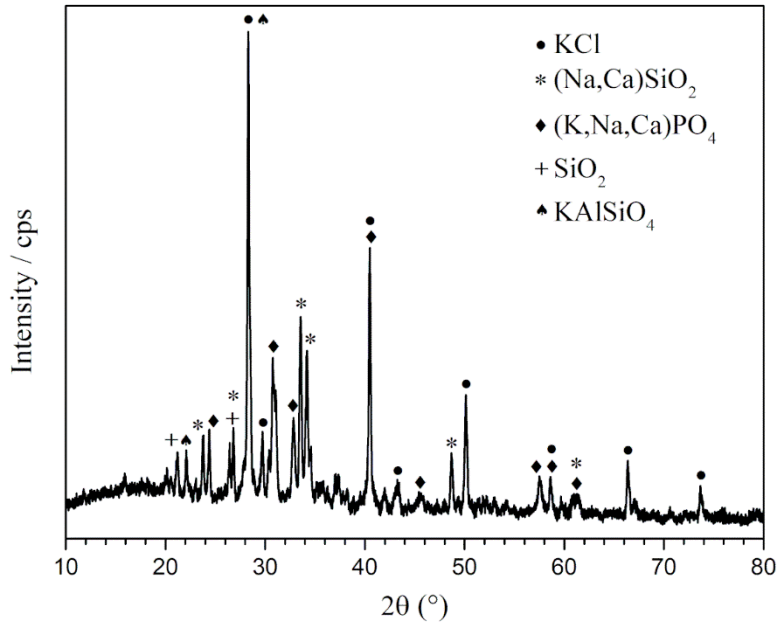


Figure 4.1 – XRD pattern obtained for the fern ashes. A heterogeneous composition is observed, with the presence of • sylvite (KCl), ∗ sodium calcium silicate ($(Na,Ca)SiO_2$), ♦ potassium sodium calcium phosphate ($(K,Na,Ca)PO_4$), + silica (SiO_2), and ♠ kalsilite ($KAlSiO_4$).

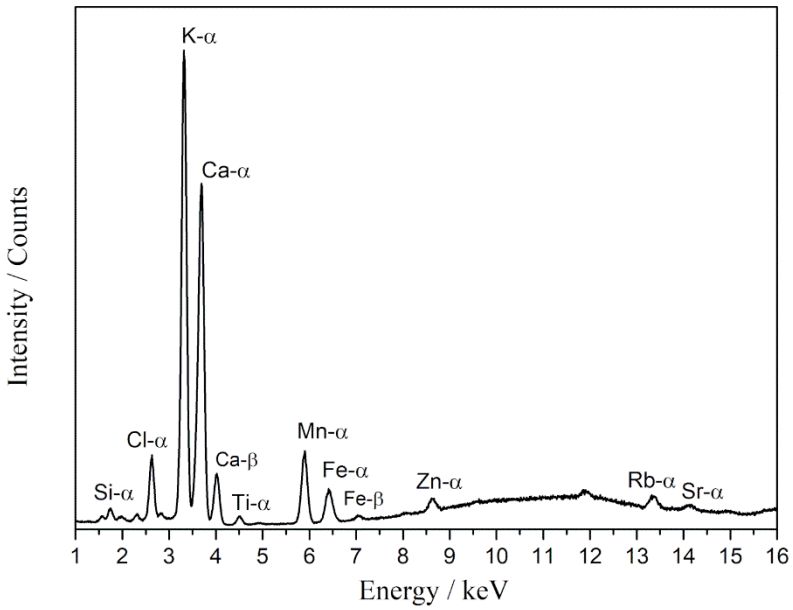


Figure 4.2 – µ-EDXRF spectrum of the salt obtained from the lixiviation of fern ashes.

Other types of ashes used from the 15th century onwards were the ones obtained from wine lees, extracted from the bottom of the wine barrels, called *tartaro* or *grumma*. These ashes, rich in potassium, would also be treated to obtain a salt rich in potassium carbonate. Cipriano Piccolpasso on his treatise *Li tre libri dell'arte del vasaio*, dated probably to 1557, describes in detail how to prepare the ashes, and also makes a curious reference to the treatment of the wine lees. Once collected, they should be taken outside the city to be burned, due to its bad smell, which could even make pregnant women miscarry (Lightbown and Caiger-Smith, 1980) (Figure 4.3).

Figure 4.3 – Piccolpasso in his treatise *I tree libri dell'arte del vasaio* (16th century) explains in detail the treatment of the wine lees[21].

In Neris' treatise, we do not see any reference to this peculiar feature. The author makes only one caution, which is that when burning the wine lees they should not be burned until they become white, otherwise "the salt will be no good" (Engle 2003, vol. I, p. 29), unlike Piccolpasso, that refers to the final product as "all the white part" (Lightbown & Caiger-Smith 1980, vol. II, p. 51). The extraction of the tartar salt described by Neri is somehow a similar procedure as the one for the salt from plant ashes: the author recommends filling the container to place the ashes with common hot water and leave it to boil until the amount of water decreases to one-quarter, and then leave it to cool to room temperature. The next step is to filter this solution, resulting on a strong lye. This lye is filtered and placed in glass containers and heated until a white salt appears at the bottom. The author then prescribes the dissolution of the said salt into a new solution of hot water and leave it undisturbed for 2 days. This step is then repeated four more times. The final product would be a salt rich in potassium carbonate.

For this work, wine lees[22] were collected and calcined on a terracotta pan at 250 ºC in a furnace, mixed with a glass spoon during the heating process. The resulting ashes were re-ashed at 850 ºC, and analysed

[21] Piccolpasso, C. (1857) *I tre libri dell' arte del vasajo*. Edited by G. Delsette and R. De Minicis. Roma: Dallo Stabilimento tipografico (https://archive.org/details/itrelibridellar00minigoog).

[22] The wine lees were obtained from a private winery production.

by XRD. As can be seen by the results obtained, the ashes obtained from the wine lees are very rich in potassium compounds, namely potassium carbonate, potassium oxide and potassium chloride (Figure 4.4).

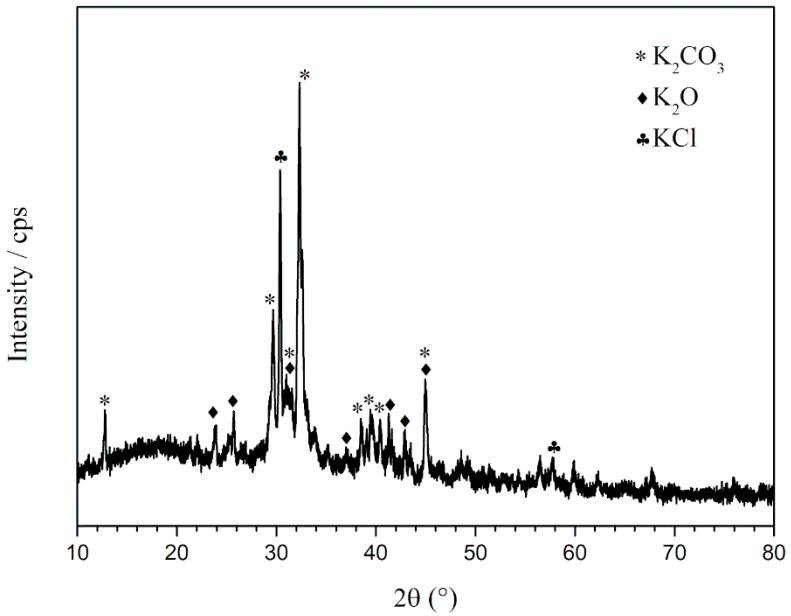


Figure 4.4 – XRD pattern for the ashes obtained from wine lees, with the presence of ∗ potassium carbonate (K_2CO_3), ♦ potassium oxide (K_2O), and ♠ potassium chloride (KCl).

The production of the blue enamel colour consisted of mixing the enamel base glass with zaffer, and also manganese or copper, to obtained different shades of blue.

Metallic oxides were added in order to colour glass with various tones. They were extracted from the mines, a process as old as the craft itself, which gained a new impulse during the Renaissance period. This craft, once monopolised by the monarchy, began to be under the control of merchants and investors. The Holy Roman Empire became the centre of mining exploitation during the Middle Ages, with three main centres stablished in the 15th century: Saxony, the Harz Mountains and Hungary (Trengove, 1965; Ball, 2007).

The production of the blue colour was prepared from the treatment of a cobalt ore. Between the 15th and 18th centuries, the main source of cobalt came from the mines in Schneeberg, in the Erzgebirge region, in particular, from the ores skutterudite, a cobalt arsenide with nickel and bismuth, and a variable amount of impurities, cobaltite or smaltite (Gratuze *et al.*, 1992, 1996). One of the first references to this mineral was made by Agricola on his treatise *Bermannus* (1530), referring to as *cobaltum*, or *kobelt*, named after a legend of *goblins* who lived in the mines and haunted the workers (Ball, 2007). This mineral was associated with other minerals, such as zinc, copper, arsenic, nickel, and bismuth, and used for the manufacture of zaffer and smalt, a blue pigment used for glass and ceramics. Its invention is attributed to the bohemian glassmaker Christopher Schürer, between 1540 and 1560 (Beckmann 1846, p.483). The extraction and treatment of cobalt were a mystery for many years. In fact, Antonio Neri on his treatise *L'Arte Vetraria* (1612) does not mention its origin, nor provides any indication of being imported; it

only mentions that prior to its use zaffer was roasted and then sprinkled with strong vinegar (Engle 2003, vol. I, p. 30). Christopher Merret on his *Art of Glass* (1662) mentions that might be an invention of "some metal-men in *Germanie*" (Merrett 1662, p. 279). The mystery regarding the preparation of this pigment is unveiled with Johann Kunckel, on his treatise *Ars Vitraria Experimentalis* (1679). Kunckel translates Neri's, adding comments and corrections to his recipes, including annotations about the preparation of zaffer, where he states that the one given by Neri was not necessary. According to Kunckel, zaffer is the result of the calcination of a cobalt ore, which results in a product rich in cobalt oxide (Holbach, 1752). He prescribes the calcination of this mineral until the white smoke (arsenic) stops to come out from the furnace. The result is grinded very roughly and then calcined a second time. After this second calcination, the final product is mixed with two parts or more of calcined pebbles. This mixture is then properly stored and exported this way (Holbach 1752, pp. 51-52).

Nevertheless, some questions remain regarding its trade. References state zaffer was a mixture of this product with a silica source such as quartz pebbles, and exported this way, in order to protect its fabrication (Holbach 1752, p. 52). Other authors state zaffer was only the calcined mineral, which could be exported with or without sand (Beckmann 1846, p. 478).

On the other hand, smalt was composed of a mixture of zaffer, sand, and potash, which could also be used as a colouring agent for blue enamels. Robert Dossie on his treatise *The Handmaid to the arts* (1758) states smalt "ground very fine, and mixt with a fourth part of its weight of borax" could be used for enamel paint (Dossie 1758, p. 254).

Two samples of skutterudite[23] ($CoAs_3$), both from Schneeberg, were analysed by XRD. The difference between the two samples is their purity, meaning that one of the samples is richer in silica (a feature seen with the naked eye). On the context of this work will be named sample a, and sample b, respectively the one richer in cobalt arsenide and the one richer in silica. The results for sample b are presented in Appendix II. The XRD pattern of sample a shows the presence of cobalt compounds, nickel and arsenic compounds (two minerals commonly associated with cobalt) and silica (Figure 4.5 and Figure II.1, Appendix II for sample b). As attested by the visual perception of both samples, sample b presents more silica than sample a. Both minerals were calcined at 1000 ºC, and the result was also analysed by XRD (Figure 4.6 and Figure II.2, Appendix II). It is possible to verify the decrease of the intensity of the peaks related with cobalt arsenide (with a possible amorphisation of the material) giving more evidence to the presence of quartz. This fact does not mean the absence of the cobalt ore, but a change in its crystalline structure, since the arsenic is lost. In addition, the formation of new compounds is observed, namely atelestite ($Bi_2O(AsO_4)(OH)$) and rammelsbergite ($NiAs_2$).

The μ-EDXRF analysis to both samples, before and after calcination, allowed to confirm this information. With the loss of some arsenic, the presence of cobalt and bismuth becomes more evident (Figure 4.7).

[23] Skutterudite ore was kindly provided by Christin Kehrer, the curator of the ore deposit and petrological collection from the University of Freiberg, Germany.

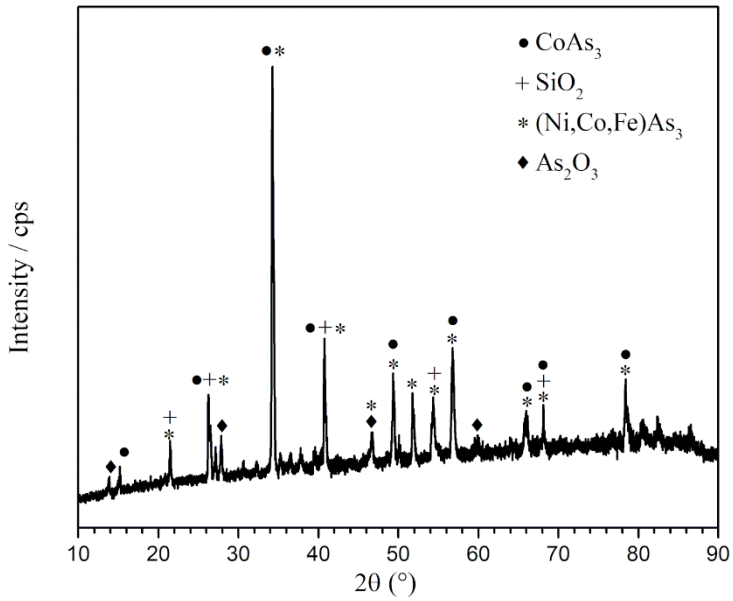


Figure 4.5 – XRD pattern for the skutterudite, sample a. • skutterudite ($CoAs_3$), + quartz (SiO_2), * nickelskutterudite ($(Ni,Co,Fe)As_3$), and ♦ arsenolite (As_2O_3).

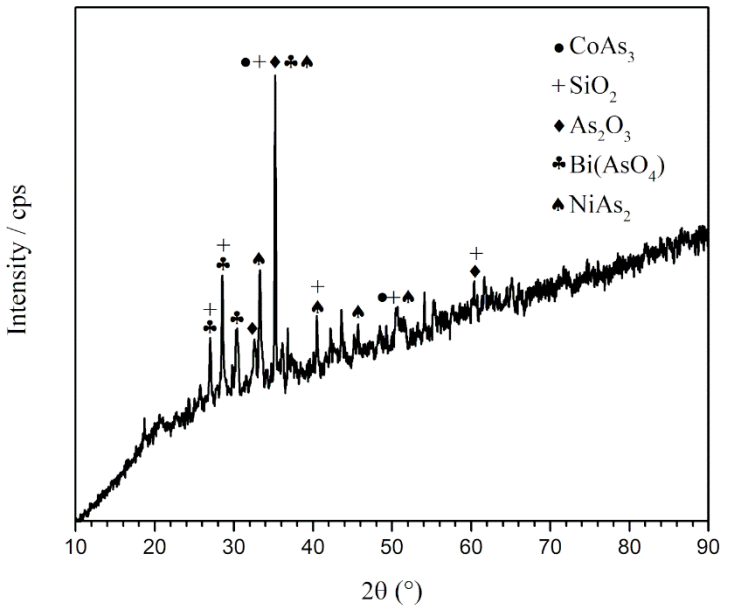


Figure 4.6 – XRD pattern for the calcined skutterudite. • skutterudite ($CoAs_3$), + quartz (SiO_2), ♦ arsenolite (AsO_3), ♣ Rooseveltite ($Bi(AsO_4)$), and ♠ Rammelsbergite ($NiAs_2$).

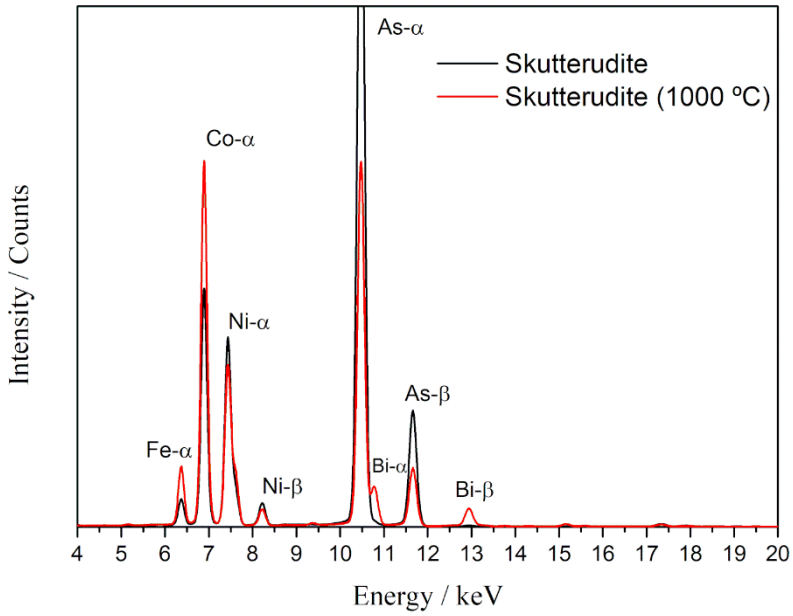


Figure 4.7 - μ-EDXRF spectrum of skutterudite (sample a), before and after calcination at 1000 ºC.

With the study and characterization of selected raw materials it was possible to establish an intersection between the information provided by the historical sources and laboratory work. The methodology which was replicated provided good results, revealing, as expected, their complexity and heterogeneity. The analyses of the Ticino pebbles confirmed their high level of silica content associated with its use for the production of glass of high quality. The mineralogical characterisation of skutterudite provided insights on the impact that it has, not only on the final glass composition, but also on the morphologic characteristics of the glass paint. As for the fern ashes, a heterogeneous composition was found, which is in accordance with the literature. However, we have to keep in mind that the chemical characterisation presently analysed is directly influenced by certain factors such as the period and place of extraction, and the type of soil.

The Handmaid to the Arts (1758): raw materials and recipes

Dossie presents in his publication thirty-nine enamel recipes for various colours: nine recipes for yellow, six recipes for green, five blue recipes, five for crimson red (called the "purple gold"), four recipes for orange, four purple recipes, four recipes for brown and two recipes for black.

For the production of these colours, the author presents four enamel base glasses, or as he called "flux", and a fifth one regarding the use of "Venetian glass, as a flux", which was produced with "wrought pieces" of Venetian glass, possibly cullet.. The author mentions that this glass could be produced in Venice or "in anywhere" (Dossie, 1758), indicating it could be a Façon-de-Venise production.

It is possible to divide the recipes into two distinct groups: one group presents lead on its composition, with the addition of "glass of lead", and the other group does not present lead on its composition. Borax ($Na_2B_4O_7 \cdot 10H_2O$) was also used, in both groups.

Dossie is the first author to describe the use of this compound for the production of enamels (Grieb, 2004). Dossie describes borax as "a salt of very peculiar qualities", stating its use was not so common, but it was of "greatest consequence to the art of enamelling" (Dossie, 1758). Earlier European references state the use of borax for glass production. Johann Kunckel, in the treatise *Ars Vitraria Experimentalis* (1679), mentions its use for the manufacture of gems (Dungworth and Brain, 2005). The term 'borax' was used in many historical references also to mention 'flux' since it was confusing to workers to differentiate the different salts, which led writers to pass the wrong information. Therefore, the mention of the term 'borax' does not always indicate the use of it in the recipes but may refer to any other salt used as a flux. Literature states borax was rarely used for enamels before the 17th century (Grieb, 2004). Finally, to apply the paint over the glass, Dossie prescribes the used of selected binding agents like oil of spike of lavender, which could be mixed with oil of turpentine to help with the paint, "in order to make them go further" (Dossie, 1758), meaning the use of these binders would result on a better paint, easy to apply.

For each enamel recipe, several base glasses could be used. The author presents a division between the base glasses and the enamel recipes. Base glasses are organized and numbered in chapter IX, section IV (Dossie 1758, pp. 273-278). This organization is important to understand the description of the enamel recipes presented in section VI of the same chapter, where for each enamel recipe Dossie refers the enumeration of the base glasses described in the previous section. These enamel recipes are also numbered. One enamel recipe can have two, three or more modifications, depending on the base glass used. Enamel recipes nº6 to 10, presented in chapter IX, section VI, are the ones for the colour blue (Dossie 1758, pp. 288-291). In chapter X, section III, Dossie describes the enamel recipes applied on glass (Dossie 1758, pp. 315-316). In this chapter, Dossie makes reference to the enamel recipes 6, 8 and 10, and therefore, these were the enamel recipes reproduced on the context of this work. Figure 5.7 presents a schematic organization of the enamel recipes reproduced, with the original enumeration of the recipes.

To obtain the colour blue, zaffer was used as a colouring agent. The author refers to zaffer as "an earth, obtained by calcining a kind of stone called cobalt", and when mixed "with proper additions; which are generally fixt alkaline salts and sand, or calcined flints", smalt could be obtained. Dossie states smalt "ground very fine, and mixt with a fourth part of its weight of borax" could also be used for enamel paint (Dossie, 1758). In order to better understand the differences between zaffer and smalt, each enamel recipe was replicated, using both colouring agents (cf. Figure 4.8).

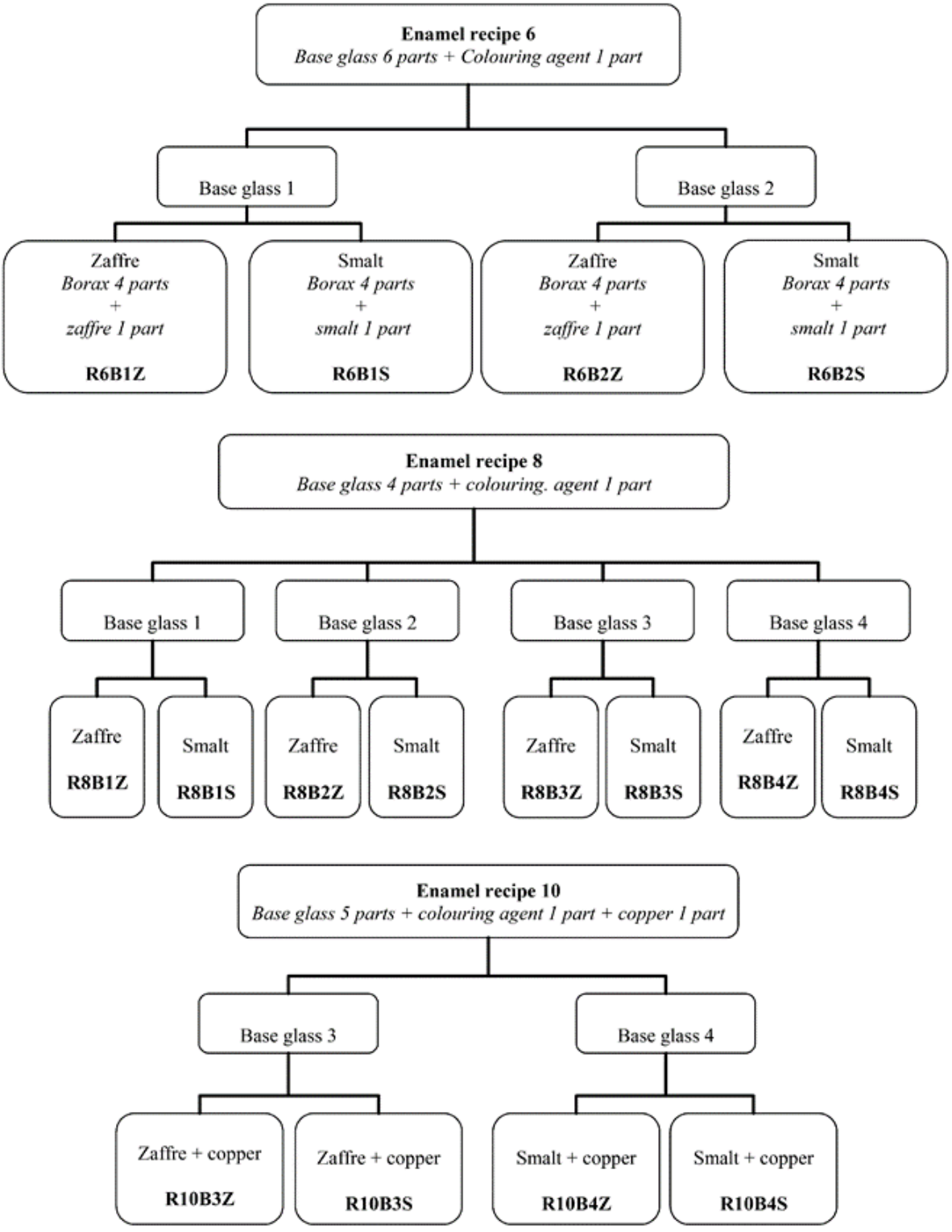


Figure 4.8 – Scheme for the organization of the enamel recipes reproduced, from Dossies' *The Handmaid to the Arts* (1758).

4.1.2. The reproductions

Antonio Neri and the reproduction of blue enamels

Blue enamels were produced with p.a. chemical reagents and fused in modern electric furnaces. That is why it is important to have in mind that the raw materials and production parameters are different from the historical recipes. From the recipes given by Antonio Neri, it was prepared a theoretical simplified recipe, from which the impurities associated with the raw materials were removed (Table 4.4). Table 4.4 presents the raw materials and their respective chemical compounds along with the composition used for the production of the blue enamel.

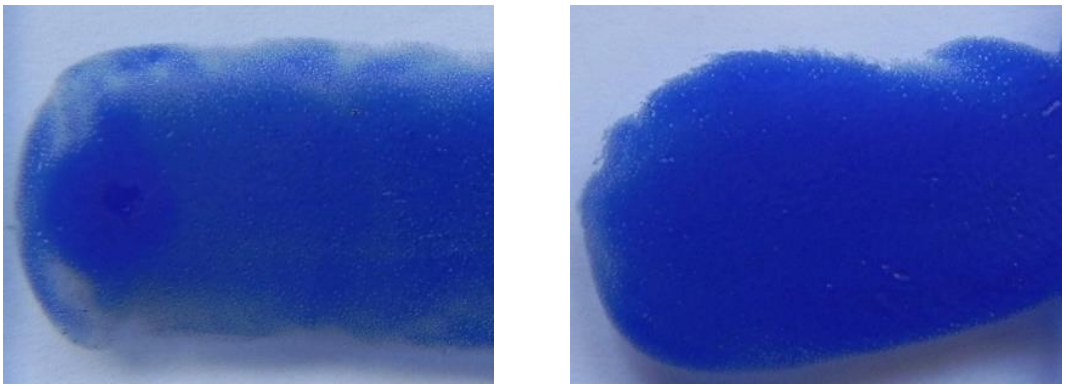
The mixture of the components (with a total of 100 g) was placed in an alumina crucible and heated at a temperature of 1200 ºC for several hours. The molten glass was poured into cold water in order to break the glass into several pieces. The obtained glass was then dried and grinded on a mechanical agate grinder, in order to obtain a fine powder to apply over the base glass.

Table 4.4 – Raw materials and respective chemical compounds used for the production of a blue enamel, according to the recipe *Altro smalto azzurro*. The composition of the blue enamel produced is also presented.

Base glass	*Cristallo* frit 50 lb	*Tarso* 200 lb	SiO_2 (w/w %) 28.6
		Polverino salt 130 lb	Na_2CO_3 (w/w %) 18.6
		Tartar salt 8 oz	K_2CO_3 (w/w %) 0.6
		Calcined lead 30 lb	PbO (w/w %) 22,5
		Calcined tin 33 lb	SnO_2 (w/w %) 24.7
Blue enamel		*Zaffera* 2 oz (0,125 lb)	CoO (w/w %) 4,8
		Ramina di tre cotte 2 pwt (0,006 lb)	CuO (w/w %) 0,2

When it comes to applying the blue enamel over the glass, Antonio Neri does not explain how to proceed. To better understand this procedure, it was necessary to explore other treatises, such as the Robert Dossies' *The Handmaid to the Arts*. In this treatise, the author states that the blue enamel can be applied to a surface (glass or other) in one of two ways. A first approach consists in the mixture of the pigment with a binder, such as lavender oil, forming a paint to apply with a brush. However, a homogeneous layer can be difficult to obtain this way. Another way to apply the paint is to apply the oil over the surface, and then to disperse the pigment over the binder, removing all the enamel pigment that does not get well attached to the surface. In both cases, the author mentions the importance of the drying time before heating, which must be short. Figure 4.9 presents the results obtained using both techniques, after annealing the enamel paint until 700 ºC, and keeping at 700 ºC for 10 minutes. According to

previous studies, these parameters showed good results (Caen, 2009). As we can observe the second method presents a more homogeneous layer resembling the type of paint that we can find in historical stained glasses.



(a) (b)

Figure 4.9 – Detailed of the application of paint, with (a) the use of a brush to apply the blue enamel, and (b) the application of the binder and further dispersion of the pigment.

Robert Dossie and the reproduction of blue enamels

For the preparation of blue enamels, p.a. chemical reagents were mixed according to the recipes. Their production was achieved step-by-step, in line with the instructions given by the author, thus, base glasses were produced, and the colouring agents were then added in order to produce the final enamel recipe. Table 4.5 presents the raw materials used to produce the base glasses, with the respective chemical reagents used in the laboratory, while in Table 4.6 the final nominal composition of each enamel recipe is presented alongside with the final measured composition obtained by µ-PIXE. The preparation and the exact amounts used to produce both base glass and blue enamel are presented in Appendix III.

Table 4.5 - Base glasses used for the reproduction of enamels.

Raw material	**Glass of lead**	**Common flint glass**	**Pearl ashes[24]**	**Sea salt**	**Borax**	**Arsenic**
Chemical reagent	*Pb_3O_4:SiO_2 2:1 (wt%)*	*SiO_2*	*K_2CO_3*	*NaCl*	*$Na_2B_4O_7{\cdot}10H_2O$*	*As_2O_3*
Base glass 1	1 lb	-	6 oz (0.375 lb)	2 oz (0.125 lb)	-	-
Base glass 2		-		-	4 oz (0.25 lb)	1 oz (0.0625 lb)
Base glass 3	-	1 lb		2 oz (0.125 lb)		-
Base glass 4	-		4 oz (0.25 lb)			2 oz (0.125 lb)

Two types of enamel recipes were prepared, varying the colouring agent: one was made with the use of zaffer, other with the use of smalt. Zaffer was prepared according to the prescription given by Kunckel

[24] Pear ash is the definition given to refined potash, obtained from the treatment of commercial potassium carbonate. The term "pearl ash" first appeared in the 18th century.

(SiO_2:CoO 2:1, w/w) (Holbach 1752, p. 52), and smalt was prepared as described by (Brady & Clauser 1989, p. 204) (71% SiO_2, 7% CoO, 21% K_2CO_3 and 1% Al_2O_3).

Table 4.6 – Nominal (N) and measured (M) composition (wt %), by µ-PIXE, of the blue enamel recipes reproduced. The enamel recipes submitted to corrosion (sub-chapter 4.1.4) are highlighted in blue.

		SiO_2	**PbO**	**K_2O**	**Na_2O**	**B_2O_3**	**As_2O_5**	**Al_2O_3**	**Cl**	**CoO**	**CuO**
R6B1Z	N	23.4	43.1	16.7	6.2	4.7			4.7	1.1	
	M	29.6	47.5	9.3	6.9	nd		5.8	<0.11	0.89	
R6B2Z	N	22.4	40.8	15.8	4.7	10.9	4.2			1.1	
	M	25.9	44.5	11.7	3.2	nd	5.2	8.3		1.00	
R8B1Z	N	32.9	37.6	14.6	3.7				4.1	7.1	
	M	36.4	41.4	9.4	4.2			2.7	<0.09	5.9	
R8B2Z	N	32.6	35.3	13.6	2.2	5.1	3.6			7.6	
	M	34.9	37.8	11.2	2.3	nd	4.6	3.0		6.2	
R8B3Z	N	69.2		14	4.2	1.3			4.1	7.2	
	M	77.3		10.1	5.5	nd		0.90	0.46	5.8	
R8B4Z	N	64.4		8.5	5.3	4.6	6.2		3.7	7.3	
	M	71.5		5.9	5.6	nd	4.6	5.7	0.86	5.7	
R10B3Z	N	58.1		12.3	3.7	1.1			3.6	4.9	16.2
	M	68.1		9.4	5.7	nd		0.95	0.49	2.7	12.7
R10B4Z	N	53.7		7.4	4.7	4.1	5.5		3.3	5	16.4
	M	61.6		5.3	3.1		5.0	4.3	0.51	4.6	15.5
R6B1S	N	23.6	43.2	17.2	6.3	4.7		0.03	4.7	0.2	
	M	27.1	46.5	9.8	11.2	nd		4.8	0.42	0.24	
R6B2S	N	22.6	40.9	16.3	4.7	11	4.2	0.04		0.2	
	M	27.3	43.4	10.1	5.2	nd	5.0	8.7		0.26	
R8B1S	N	34.3	38.2	17.9	3.7			0.2	4.2	1.5	
	M	40.3	38.9	11.9	4.9			2.5	<0.08	1.6	
R8B2S	N	34.1	35.8	17.2	2.2	5.1	3.7	0.2		1.6	
	M	38.4	36.5	13.0	2.8	nd	4.2	3.4		1.7	
R8B3S	N	71.2		17.3	4.3	1.3		0.2	4.2	1.5	
	M	79.4		12.6	4.8	nd		1.1	0.59	1.5	
R8B4S	N	66.3		11.7	5.4	4.7	6.3	0.2	3.8	1.6	
	M	76.0		8.5	4.2	nd	3.5	5.6	0.40	1.8	
R10B3S	N	59.4		14.6	3.8	1.1		0.1	3.7	1	16.3
	M	68.0		11.4	3.6	nd		0.98	0.49	1.2	14.3
R10B4S	N	54.9		9.7	4.7	4.1	5.5	0.2	3.3	1.1	16.6
	M	62.5		6.6	4.3	nd	4.1	6.5	0.38	1.3	14.4

R: enamel recipe; B: base glass; S: smalt; Z: zaffer

For each enamel recipe, several base glasses could be used. Following Dossie, for enamel recipe nº6, base glasses nº1 and 2 were used, for enamel recipe nº8, base glasses nº1, 2, 3 and 4, and for enamel recipe nº10, base glasses nº3 and 4. Therefore, the present work comprises 16 blue enamel recipes: 8 enamel recipes with the use of zaffer and 8 enamel recipes with the use of smalt.

For enamel recipe nº6, one part of the colouring agent was added to six parts of the base glass. Also as prescribed, the colouring agent is mixed with 4 times its weight of borax. For enamel recipe nº8, four parts of the base glass were added to one part of the colouring agent.

For enamel recipe nº10, five parts of the base glass were mixed with the colouring agent and copper oxide, both one part (cf. Figure 4.8). The powders (both base glass and later blue enamel powder) were placed on a turbula for 30 minutes to obtain a homogeneous mixture. The batches were placed on a Termolab electric furnace at a temperature of 1200 ºC for 10 hours, with a heating rate of 5 ºC/min until 1200 ºC, after which were poured into cold water to make frit. The glass was mechanically grinded on a mortar grind Retsch RM 200, for 30 minutes. The resulting enamel powders were properly stored in polyethylene bags inside a desiccator with a controlled relative humidity.

Each enamel powder was mixed with oil of lavender (as prescribed by the author) from Lefranc & Bourgeois and distilled turpentine from Winsor & Newton. The paint was applied over the non-tin side of a sheet of float glass (Saint Gobain), ca. 10 cm x 2,5 cm. For each enamel paint, two reproductions were executed: one with the help of a spatula, in order to create a thick layer over the glass, other with a Zehntner 4-sided applicator frame, to apply a homogeneous layer with a thickness of 200 µm.

The reproductions were placed in a furnace at a temperature of 700 ºC, with a heating rate of 5 ºC/min, staying at 700 ºC for 10 minutes; according to previous studies, these parameters showed good results (Caen, 2009).

The blue enamels reproduced with the use of zaffer and smalt are presented in Table 4.7. All recipes where zaffer was used as colouring agent lead to a deeper blue, as expected since the content of cobalt is higher in these samples (see Table 4.6). Looking to the results obtained after firing the enamel paints it is possible to notice that some did not vitrify properly under the same heating conditions. In particular, enamels with lead-containing base glass present better-vitrified paints, while lead-free enamels present a matte surface, indicating that the enamel did not fuse properly.

Table 4.7 - Final results for each enamel recipe reproduced in this work, with the use of zaffer and smalt as a colouring agents.

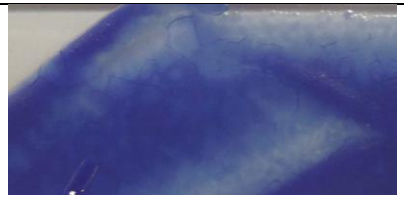
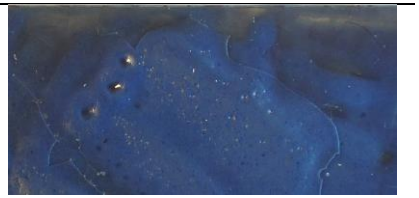
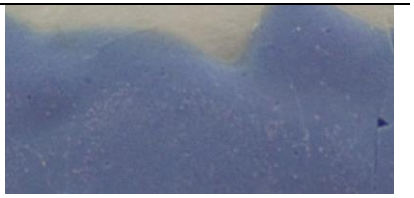
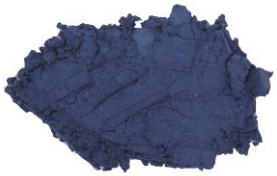
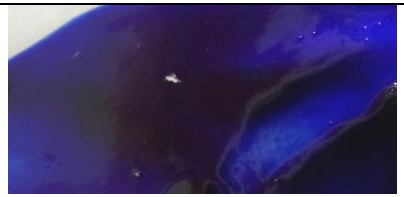
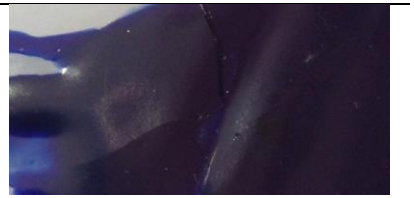
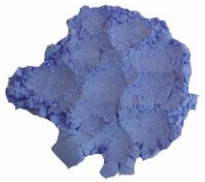
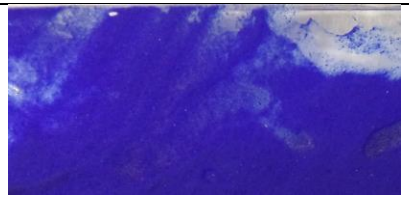
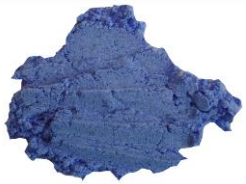
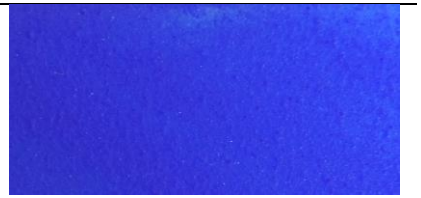
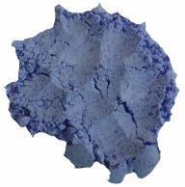
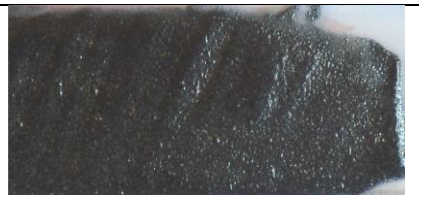
Enamel Recipe	**Colouring agent**	*Enamel Powder*	*Enamel Paint*	**Enamel Recipe**	**Colouring agent**	*Enamel Powder*	*Enamel Paint*
R6B1	Zaffer			R6B2	Zaffer		
	Smalt				Smalt		
R8B1	Zaffer			R8B2	Zaffer		
	Smalt				Smalt		

Table 4.7 – Final results for each enamel recipe reproduced in this work, with the use of zaffer and smalt as a colouring agents (continue).

Enamel Recipe	Colouring agent	*Enamel Powder*	*Enamel Paint*	Enamel Recipe	Colouring agent	*Enamel Powder*	*Enamel Paint*
R8B3	Zaffer			R8B4	Zaffer		
	Smalt				Smalt		
R10B3	Zaffer			R10B4	Zaffer		
	Smalt				Smalt		
							

For the recipes nº 6 (R6B1 and R6B2), a lighter blue was achieved both with zaffer and smalt, as expected, since the colouring agent is mixed with four times its weight in borax, as prescribed, therefore the amount of cobalt is low. It was possible to attest that the paint produced with this recipe does not present a good adhesion and the enamel easily detaches from the surface. It exhibits a matte appearance, and when smalt was used, an irregular texture was always obtained.

For enamel recipes nº 8, the results are independent of the colouring agent but vary with base glass used. For enamels with base glass nº 1 and nº 2 (R8B1 and R8B2), a well-vitrified surface is obtained, with the typical craquelure present in enamel painting on historical stained glass (Caen, 2009). For the recipes with base glass nº 3 and nº 4 (R8B3 and R8B4), the enamel presents an opaque and matte surface, possibly indicating an incomplete fusion of the paint layer. As for the enamels nº 10 (R10B3 and R10B4), two different green hues were obtained with both colouring agents, probably due to the presence of copper in their compositions. The enamel paint with base glass nº3 presents a more vitreous and shiny surface when compared with the one prepared with base glass nº4, which presents a matte appearance. Regarding the use of copper in the enamel recipes nº 10, the author mentions that this recipe "verges more towards the green, than in proportion to the warmth of nº8" (Dossie 1758, p. 316).

FORS analyses were performed on both enamel powder and enamel paint. The obtained UV-Vis spectra are presented in Figure 4.10 (enamels R6 and R8) and in Figure 4.11 (enamels R10).

According to with the literature, Co^{2+} in tetrahedral coordination presents due to the Jahn-Taller effect a triple band at 540, 590 and 640 nm in the visible region, corresponding to the transitions $^4\Gamma_2 \rightarrow {}^4\Gamma_5$, $^4\Gamma_2 \rightarrow {}^4\Gamma_4$ and $^4\Gamma_2 \rightarrow {}^4\Gamma_4$ *(P)*, respectively (Navarro, 2003). Previous studies performed on two samples of blue stained glass from the 15th century allowed to correlate the position of the Co^{2+} peaks and the chemical composition of the glass (Bacci and Picollo, 1996; Bacci *et al.*, 2007). The samples analysed were K-rich blue glass, presenting a Co^{2+} triplet band at 540, 601 and 652 nm. Other study performed on Na- and Ca/K-rich glass of roman, post-medieval and industrial period observed for Na-rich glass a Co^{2+} triplet placed at 534.7, 595.1 and 644.5 nm, and 526.5, 595.5 and 648.4 nm for Ca/K-rich glass (values calculated from an average of samples available) (Ceglia *et al.*, 2012).

For the blue enamel recipes R6 and R8, the first band of the Co^{2+} triplet of the produced enamels before and after firing is centred between 531 nm and 546 nm, the second 594 – 600 nm and the third 647 – 656 nm. There is no evident relation between composition type - the enamels produced can be classified as lead glass when PbO > 15 wt % or mixed-alkali when K_2O/Na_2O > 0.6 wt % (Schalm *et al.*, 2007) – and the obtained UV-Vis spectra. It is, however, important to notice that in some cases after the firing, variations in the intensity of the bands did occur. These alterations are probably associated with rearrangements of the glass network.

For the blue enamel recipes R10 (Figure 4.10), the UV-Vis spectra clearly display the presence of not only Co^{2+} but also of Cu^{2+}. The difference between the powders and the fired enamels is evident for all cases, but more pronounced for the enamel R10B4Z and R10B4S.

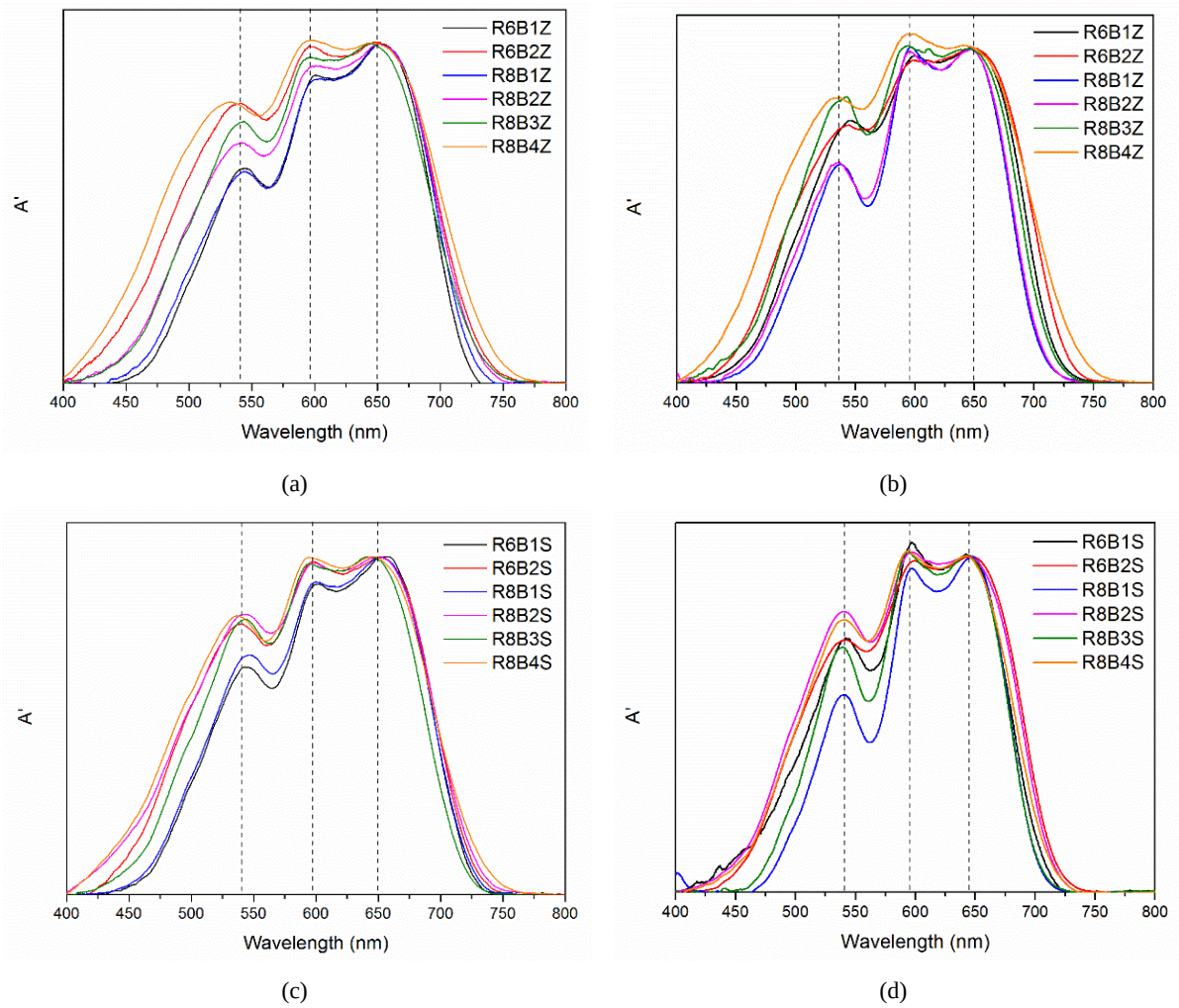


Figure 4.10 - Absorption spectra of enamel paints 6 and 8, with the use of zaffre and smalt: (a) and (b) spectra for the enamel powder and enamel paint with the use of zaffre, respectively, (c) and (d) spectra for the enamel powder and enamel paint with the use of smalt, respectively. The spectra were normalized to the third band of the cobalt triplet.

For the enamel powder with base glass nº3 (Figures 4.10a and 4.10c, green line) is possible to verify the presence of the triple band of Co^{2+}, and a broader band situated around 720 nm and at least 1050 nm, corresponding to the $^{2}\Gamma_{3}\,(F) \rightarrow {}^{2}\Gamma_{5}$ transition of octahedral coordinated Cu^{2+}. This absorption band is shifted towards higher wavelengths when compared with the literature (Navarro, 2003). This tendency might occur due to the enamel composition which presents a high alkali content (K_2O+Na_2O content between 20-23 wt% for base glass nº3 and 16-19 wt% for base glass nº4). This fact might also explain the hue, from green (R10B4) to blue (R10B3) since the ratio CoO:CuO is identical for both recipes.

Furthermore, the spectra of the enamel recipes R10B4 (Figures 4.10a and 4.10c, orange line), shows an absorption cut-off around 450 nm. This can be related to a possible conversion of a part of Cu^{2+} ions into Cu^{+} ions due to the presence of arsenic oxide, which may alter the oxidation state of colouring ions (Shelby, 1997).

When looking to the absorption spectra of the enamel paints, the difference between base glass nº3 and nº4 becomes more evident. The spectra for base glass nº3 (for both colouring agents) reveals the presence of Co^{2+} triplet, but the absorption band of Cu^{2+} seems to be almost absent.

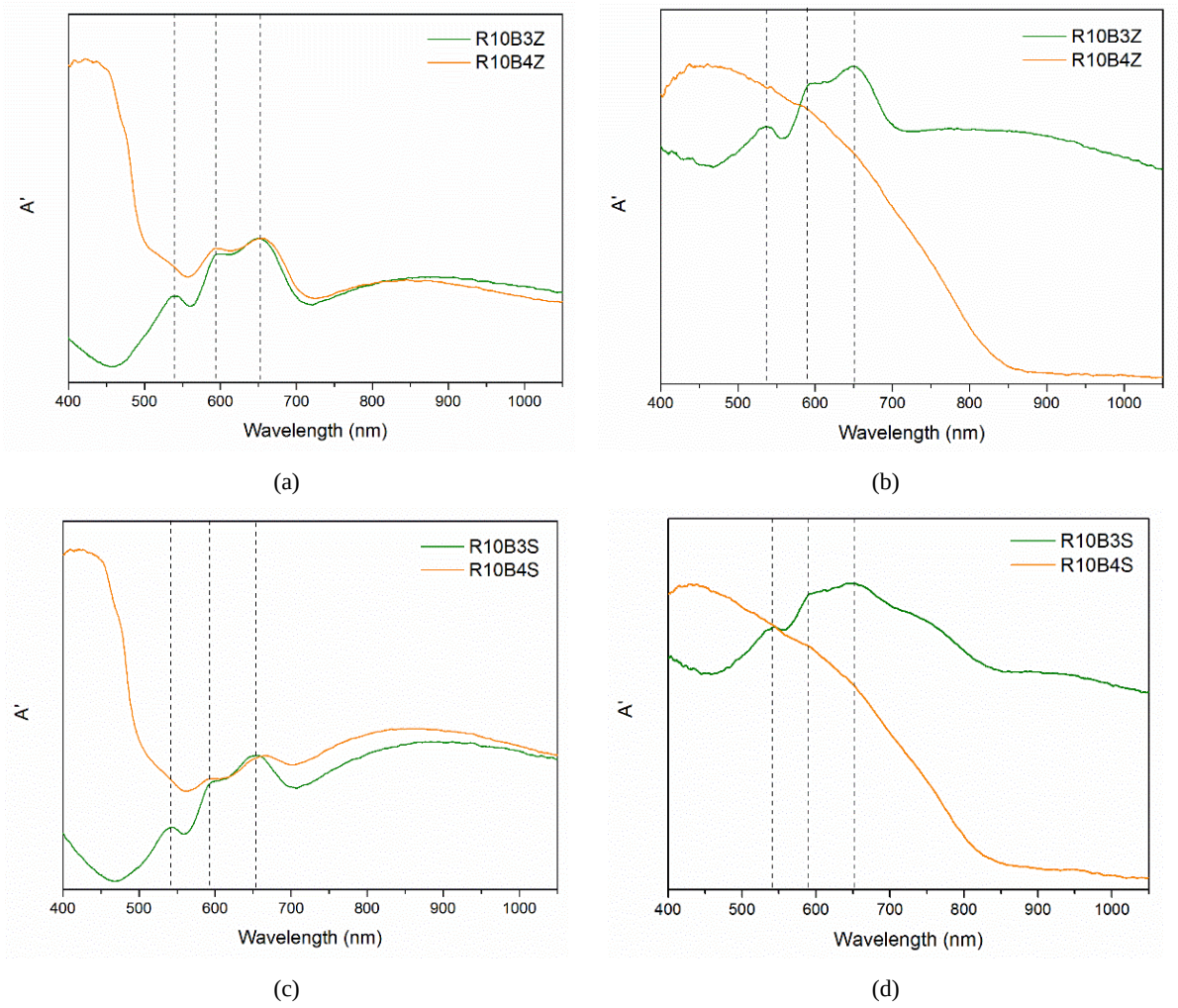


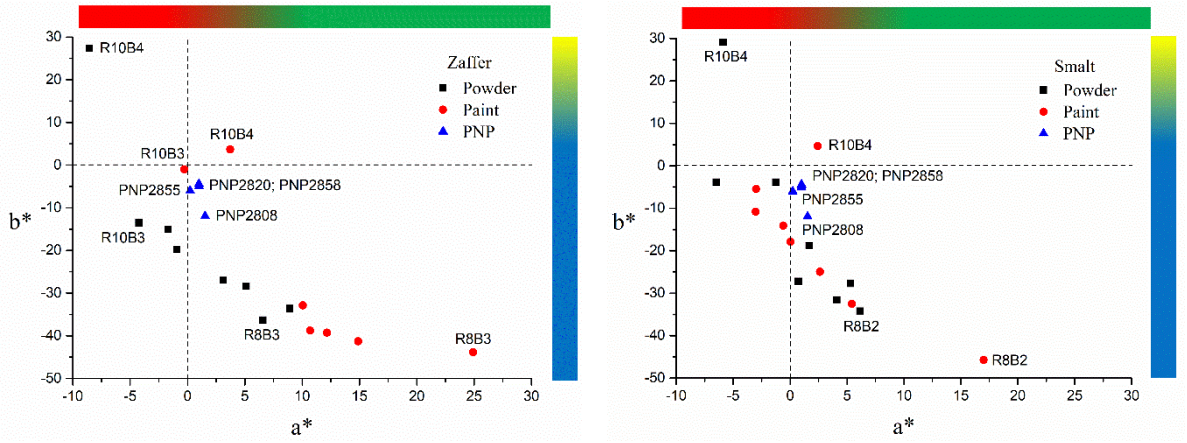
Figure 4.11 - Absorption spectra of enamel paints 10, with the use of zaffre and smalt: (a) and (b) spectra for the enamel powder and enamel paint with the use of zaffre, respectively, (c) and (d) spectra for the enamel powder and enamel paint with the use of smalt, respectively. The spectra were normalised to the third band of the cobalt triplet, with the exception of the enamel paints R10B4Z and R10B4S.

The absorption spectra of the enamel paint with base glass nº4 for both colouring agents reveals one single and not well-defined cut-off.

Colorimetric measurements using the Lab* system were performed, with the acquisition of Lab* (Table 4.8) and *xy* coordinates (Figure 4.12). As expected, measurements on the blue enamels gave negative values for *b**, being more negative in the case of the enamels produced with zaffer, a result seen for both enamel powder and enamel paint. Also for enamel paint with smalt as a colouring agent, it is possible to perceive higher *L** values. A result which is predictable, since smalt has a lower CoO amount, therefore the colour is lighter. Values for *b** coordinate for enamel recipes nº10 gave positive values, verging towards yellow, in combination with negative a* values, indicating a greener colour.

Figure 4.12 presents the a* vs. b* coordinates of the recipes with the use of zaffer and smalt. It is possible to notice a more identical distribution of colour of the powders and final paints in the recipes with the use of smalt. This can indicate that smalt is more stable at high temperatures when compared with zaffer,

being possible to predict the final colour. This is probably associated with the fact that smalt is already a powdered glass while zaffer is only a mixture of CoO and silica.



(a) (b)

Figure 4.12 – a* vs. b* chart of the enamel paints with the use of (a) zaffer and (b) smalt as colouring agents. The results for stained glass samples are also presented.

Colorimetric measurements were also performed on blue enamel painting from four stained-glass panels from Pena National Palace, dated to between the 16th and 17th centuries.

Looking to the colorimetric diagram and the position of stained glass panels' case study, they reveal a more similar behaviour with the enamel paints with the use of smalt as a colouring agent (cf. Figure 4.12).

Table 4.8 – Lab* coordinates for the blue enamels reproduced, with the use of zaffer and smalt as colouring agent.

Recipe		Enamel Powder			Enamel Paint		
		L*	**a***	**b***	**L***	**a***	**b***
Zaffer	**R6 B1**	69.57	-1.7	-15.07	21.5	14.9	-41.27
	R6 B2	68.7	5.13	-28.43	43.93	10.7	-38.77
	R8 B1	54.4	-0.93	-19.73	23.17	31.6	-61.1
	R8 B2	58.77	3.13	-26.97	19.67	10.07	-32.9
	R8 B3	53.57	6.57	-36.3	19.17	24.93	-43.87
	R8 B4	55.1	8.93	-33.63	55.7	12.17	-39.27
	R10 B3	59.17	-4.23	-13.53	22.53	-0.27	-1.03
	R10 B4	51.2	-8.57	27.4	20.87	3.73	3.67
Smalt	**R6 B1**	84.27	-1.27	-3.87	25.77	-0.6	-14.1
	R6 B2	81.07	1.67	-18.77	47.02	5.43	-32.53
	R8 B1	61.47	0.73	-27.2	24.13	-3.03	-10.83
	R8 B2	62.7	6.13	-34.2	30.57	17	-45.73
	R8 B3	64.8	4.1	-31.63	26.6	0.03	-17.93
	R8 B4	64.87	5.33	-27.73	60.8	2.63	-24.97
	R10 B3	64.6	-6.5	-3.87	17.77	-3	-5.47
	R10 B4	52.7	-5.9	29.07	30.13	2.43	4.67

In addition to FORS, the enamel paint samples were analysed by Raman spectroscopy. For all the recipes R6 and R8 with the use of zaffer and smalt as colouring agents (Figure 4.13, and Appendix IV), it is possible to verify the presence of a band centred between 420 cm^{-1} and 520 cm^{-1} corresponding to the Si-O-Si bending vibrations (Robinet, Bouquillon and Hartwig, 2008). No direct relationship can be made between the composition of the enamel and the shift of the band towards higher wavelengths.

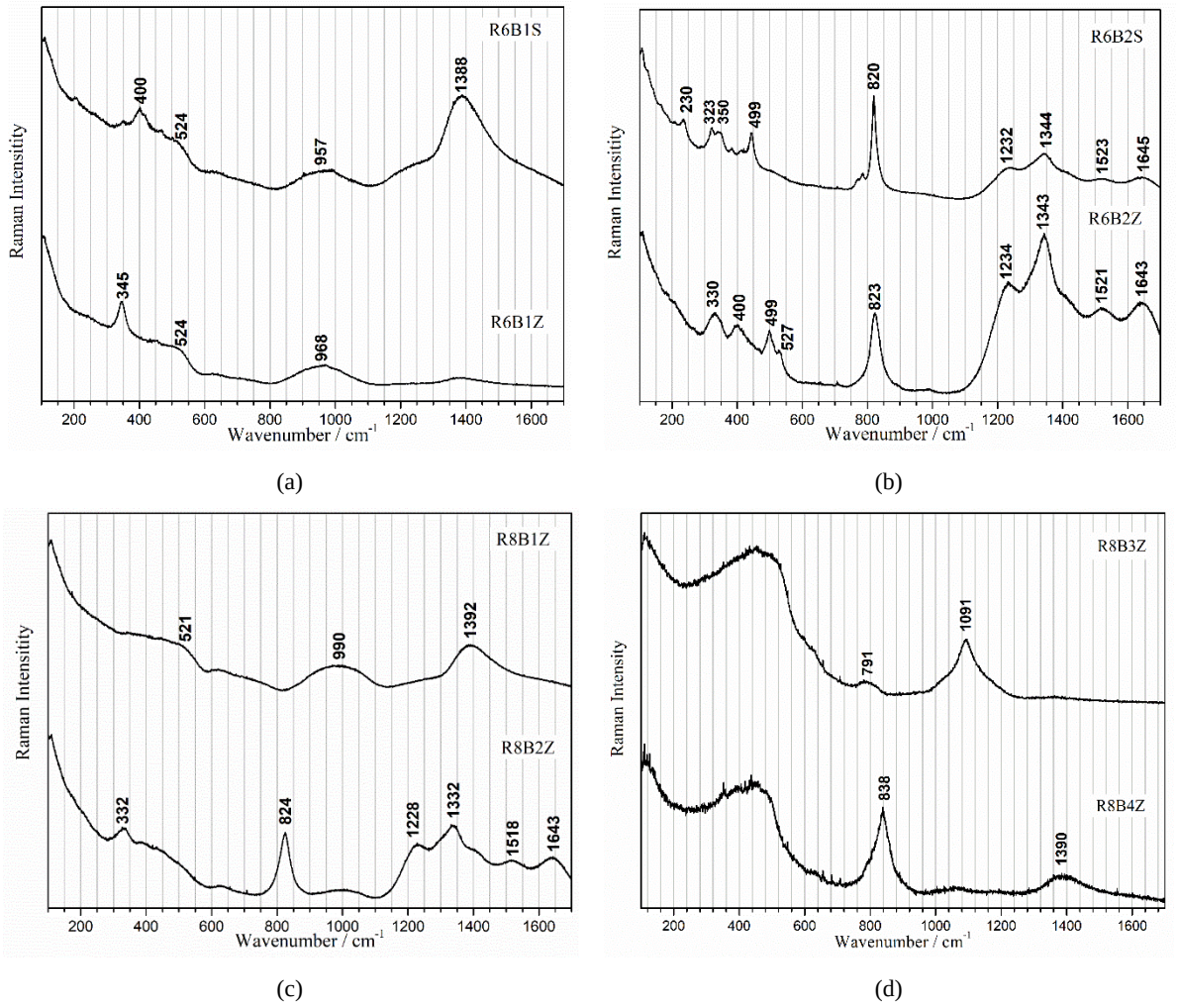


Figure 4.13 – Raman spectra of selected painted samples, (a) enamel recipes R6B1, (b) R6B2, (c) enamel recipes R8B1Z and R8B2Z, and (d) R8B3Z and R8B4Z. Raman spectra of enamel recipes R8 with the use of smalt present similar results.

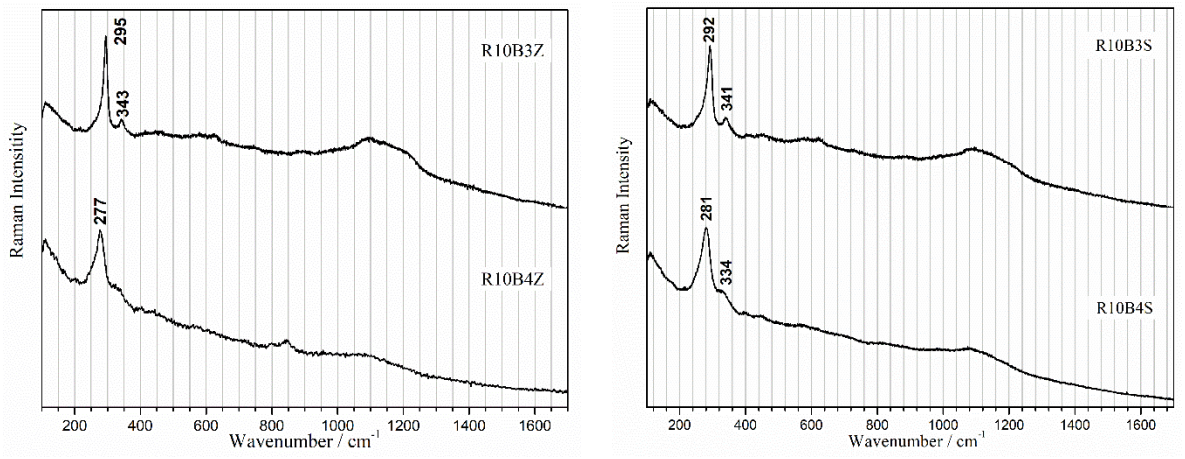
The enamel samples R6B1, R8B1, and R8B2, with the use of both colouring agents, present a broad band centred between 960 cm^{-1} and 1000 cm^{-1}, corresponding to the $Si\text{-}O^-$ stretching vibration from Q^2 species. This band is related with a high lead content present on silicate glasses (Robinet, Bouquillon and Hartwig, 2008). Enamel samples R6B1 present a higher lead content than the enamel samples R8B1 and R8B2, which explains the shift of the band towards lower wavelengths (Robinet, Bouquillon and Hartwig, 2008).

Along with the identification of the silicate network, it is also possible to assess the presence of cobalt silicate (Co_2SiO_4) on six of the enamel paints reproduced (R6B2S, R6B2Z, R8B2S, R8B2Z, R8B4S and R8B4Z), with the presence of the typical band centred between 820 cm^{-1} and 840 cm^{-1} for our painted

samples. This peak is a result of the saturation of the pigment on the glass matrix (Colomban, Milande and Le Bihan, 2004; de Waal, 2009). The enamel recipes R8B3S and R8B3Z also present a week band centred around 792 cm^{-1}, which can also be related to the presence of Co_2SiO_4. A relationship between the increase of intensity of this band and the decrease of the amount of SiO_2 on the composition is observable.

For all the enamel paints with exception of R6B1Z and R8B3Z, is possible to identify amorphous C, with the presence of Raman bands between 1220 cm^{-1} and 1640 cm^{-1} (de Waal, 2009).

For enamel paint samples R10B3 and R10B4 with the use of zaffer and smalt as colouring agents, it is possible to notice a shift of bands assignments towards lower wavenumbers for both recipes with base glass 4 (Figure 4.14).



(a) (b)

Figure 4.14 – Raman spectra of painted samples with enamel recipes R10, with the use of (a) zaffer and (b) smalt.

The sharp band centred between 280 cm^{-1} and 295 cm^{-1} corresponds to the Cu-O A_g lattice mode of Cu-O vibration. The band centred between 330 cm^{-1} and 340 cm^{-1} corresponds to the B_g lattice mode of Cu-O vibration. This band is very weak for enamel recipes R10B3S and R10B3Z and a shoulder band for enamel recipes R10B4S and R10B4Z (Goldstein *et al.*, 1990; Hagemann *et al.*, 1990).

4.1.3. Blue enamel painting from stained glass fragments from Pena National Palace and Vitrocentre Romont collections[25]

Selected stained-glass fragments from the Swiss group of the Pena National Palace collection were chosen for glass and glass-painting analysis. This group of fragments was compared with the results

[25] The content of this sub-chapter is published in: Machado, A. *et al.* (2017) 'Swiss Kabinettscheiben from a 19th century Portuguese collection. Study and chemical characterisation', in Wolf, S. and Pury-Gysel, A. de (eds) *Annales du 20e Congrès de l'Association International pour l'Histoire du Verre, Fribourg/Romont, 7-11 Septembre 2015*. Romont: AIHV - Association Internationale pour l'Histoire du Verre, pp. 684–688; Machado, A. *et al.* (2017) 'Swiss Stained-Glass Panels: An Analytical Study', *Microscopy and Microanalysis*, 23(4), pp. 878–890. DOI: 10.1017/S1431927617000629.

obtained for a group of fragments belonging to the Vitrocentre Romont. The total of 21 samples selected for were taken from small fragments belonging to stained-glass panels of these two collections: the first set of six samples from the Pena National Palace collection (PNP set), the second set comprising fifteen samples from Vitrocentre Romont (VCR set). The PNP samples were taken from fragments which were found after the restoration of their respective stained-glass panels and were thus not included in the restored panels, which were already on display when the missing fragments were discovered (cf. Figure 2.8). This was a good opportunity to study their glass composition. The VCR samples come from a collection of loose stained-glass fragments, which are part of the bequest of Hans Meyer, a stained-glass painter who worked in Zurich between 1893 and 1961. Hans Meyer also restored '*Wappenscheiben'*, and for this purpose had collected fragments of broken or discarded historic stained-glass panels (Schneider, 1978). The selection of fragments was based on their typology and the painting techniques applied, which are specific to a region and period and therefore allow an attribution of date and Swiss provenance (Lehmann, 1941; Boesch, 1955).

Description of the fragments from the Pena National Palace

This set (Figure 4.15, Table 4.9) consists of six fragments of colourless stained glass, painted with grisaille, yellow silver stain and blue enamel. One of the fragments (PNP16) also includes an area with red flashed glass (glass consisting of a thin layer of red glass over a layer of colourless glass). The grisaille is always applied to the front of the stained glass, while the yellow silver stain and the blue enamel are applied to the back.

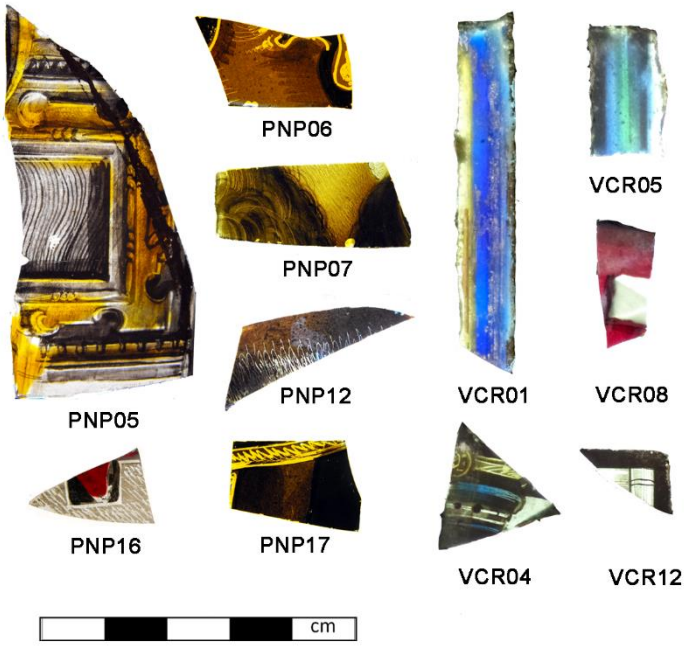


Figure 4.15 – Material analysed: the six stained-glass fragments from the collection at Pena National Palace (PNP), and five of the fifteen fragments from the collection at Vitromusée Romont (VCR).

Sample PNP05 probably belongs to the heraldic panel with the coat of arms of the canton of Luzern dating to 1688 (cf. Figure 2.8b). However, it is also possible that it was part of the panel inscribed with Ioannes Heinricus Fleischlin, which also dates to 1688 (PNP2820) (cf. Figure 2.8c); both panels originally come from the church of St. Gallus and Otmar in Kriens, Luzern. Sample PNP16 comes from panel PNP2860, a 17th-century heraldic panel with the coat of arms of Niedersimmental (cf. Figure 2.8a). PNP17 has also been attributed to the aforementioned panel PNP2820. Samples PNP06, PNP07 and PNP12 could unfortunately not be attributed to any of the existing panels in the collection. These fragments might have originated in one or more panels, which are known to have been lost from the collection. However, they may also have been used as stopgaps during a past restoration of the extant panels and subsequently been removed. There is evidence of such use of historic fragments as stopgaps within the collection. For example, panel PNP2860 (cf. Figure 2.8a), contains pieces, which probably originated in several other lost historic stained-glass panels. While the precise origins of samples PNP06, PNP07 and PNP12 are unknown, the design and painting techniques they exhibit leave no doubt that they are Swiss and date to the Early Modern Period.

Table 4.9 – Set of stained-glass fragments from Pena National Palace analysed by μ-PIXE and SEM/EDS.

Stained-glass panel	Glass colour and paints	Sample
PNP2808, *Heraldic panel with the coat of arms of the canton of Luzern* 1688 (inscribed)	Colourless glass painted with grisaille and yellow silver stain	PNP05*
PNP2820, *Ioannes Henricus Fleischlin* 1688 (inscribed)	Colourless glass painted with grisaille, yellow silver stain and blue enamel	PNP17
PNP2860, *Heraldic panel with the coat of arms of Niedersimmental* 17th century	Colourless painted with grisaille and red flashed glass	PNP16
Unknown or lost stained-glass panels 16th and 17th centuries	Colourless glass painted with grisaille and yellow silver stain	PNP06
	Colourless glass painted with grisaille	PNP07
	Colourless glass painted with grisaille, yellow silver stain and blue enamel	PNP12

*PNP05 might also be attributed to the panel PNP2820.

Description of the fragments from Vitrocentre Romont

This set (cf. Figure 4.15, Table 4.10) includes eleven stained-glass fragments consisting of colourless glass painted with grisaille, yellow silver stain and/or blue enamel (Table 4.10, VCR01-08 and VCR11-13). One of the fragments is also painted with sanguine red (VCR06), a pigment obtained from red iron oxide, which can be applied either as a transparent wash or an opaque colour. Two of the colourless fragments also include areas of red flashed glass (VCR07 and VCR08). The set also includes four coloured glass fragments. The purple coloured glass (VCR09, VCR14, and VCR15) is composed of red and blue flashed glass and the light brown glass (VCR10) consists of colourless and purple flashed glass. Two of the coloured glass fragments are painted with grisaille. As with the fragments from Portugal, the

grisaille is applied to the front of the glass, and the yellow silver stain, blue enamels and sanguine are applied to the back.

Table 4.10 – Stained-glass samples from Vitrocentre Romont analysed by µ-PIXE and SEM-EDS.

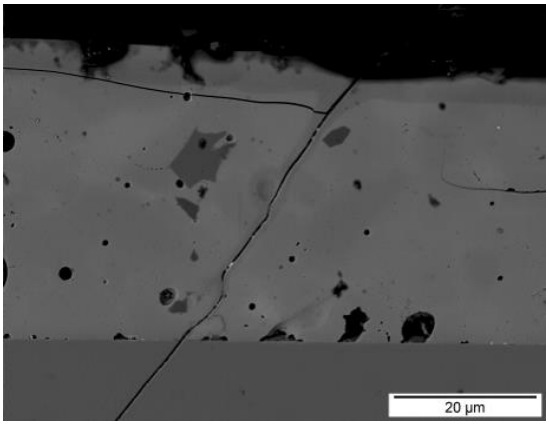
Sample	Glass colour and paints
VCR01	Colourless glass painted with grisaille and blue enamel
VCR02	Colourless glass painted with blue enamel
VCR03	Colourless glass painted with grisaille, yellow silver stain and blue enamel
VCR04	
VCR05	Colourless glass painted with grisaille and blue enamel
VCR06	Colourless glass painted with grisaille and red sanguine
VCR07	Colourless glass painted with grisaille, and red flashed glass
VCR08	
VCR09	Purple glass consisting of blue and red flashed glass, painted with grisaille
VCR10	Light brown glass consisting of colourless and purple flashed glass, painted with grisaille
VCR11	Colourless glass painted with grisaille
VCR12	
VCR13	
VCR14	Purple glass consisting of blue and red flashed glass
VCR15	

In order to determine the compositions of the bulk glass and the glass paints, and for a better assessment of the morphological characteristics of the paint layers, we took small samples (approx. 5 mm width) from the stained-glass fragments. The samples were analysed by µ-PIXE and by SEM-EDS; the latter method was also used to measure the elemental distribution (X-ray maps) and to show the structural characteristics of the paint layers (backscattered electron image mode (BSE)). For the glass paints, the results of the chemical analysis are based on the mean average of three measurements per measurement spot.

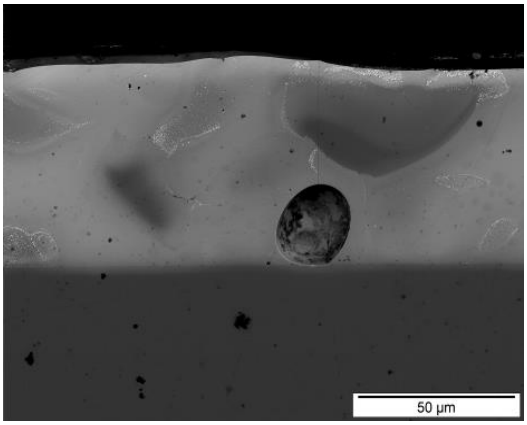
The results obtained for the bulk glass are published in Machado, Wolf, et al. (2017) (Table V.1, Appendix V). According to the literature (Schalm *et al.*, 2007; Wedepohl and Simon, 2010), the compositions of the glass—comprising the samples from both sets—can be subdivided into two groups: the first group, which includes 13 samples, has a high lime–low alkali composition (HLLA), with a K_2O/CaO ratio between 0.2 and 0.4. The second group, comprising six samples, is composed of a potassium-rich glass with high calcium content, with a K_2O/CaO ratio between 0.6 and 1.2 and a concentration above 9.5 wt. % for both K_2O and CaO. One sample (PNP06) stands out for its very high potassium and lower calcium concentration (19.4 wt. % of K_2O and 8.6 wt. % of CaO), another sample (VCR06) for its elevated sodium content (8 wt. % Na_2O and a K_2O/Na_2O of 0.3).

The glass paints, namely the blue enamel and the grisaille (which will be discussed in the sub-chapter 4.3.3), from some of the stained-glass fragments from both sets were analysed by SEM/EDS using BSE

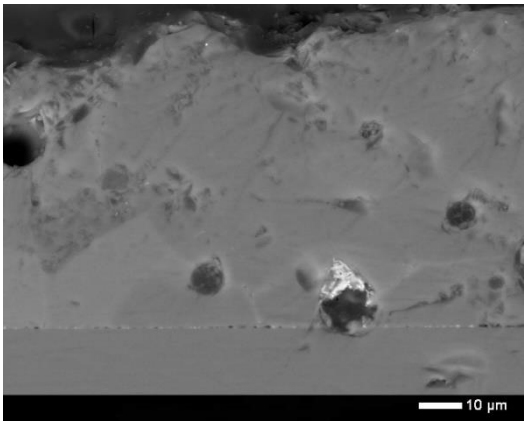
images, and by μ-PIXE in order to study morphology and composition of the paint layers. The results of the chemical analysis are based on the mean average of three measurements per measurement spot.
Figure 4.16 shows representative examples of the analysed blue enamels. The enamel layers are heterogeneous and include various glassy phases, bubbles, and inclusions that are rich in silicon and aluminium; the inclusions are probably quartz and feldspar grains. The thickness of the enamel layer ranges between approximately 30 μm and 80 μm; the thicknesses can vary within the same layer. The interface between the enamel and the base glass is well defined for all the samples, with exception of sample VCR03. This sample stands out because it has a more diffuse interface and a more homogeneous enamel layer (*cf.* Figure 4.16b).



(a)



(b)



(c)

Figure 4.16 – SEM/BSE images of blue enamels (a) VCR02, (b) VCR03 and (c) PNP12.

Small white spots are present throughout the enamel; in some cases, they follow the same patterns of some of the glassy phases, as can be seen on the enamel from sample VCR03. White angular inclusions of a size similar to the quartz and feldspar grains were observed in some samples (cf. Figure 4.16c). EDS analyses of these inclusions revealed high levels of arsenic and nickel (Figure 4.17). A similar result was obtained for the characterization of calcined skutterudite, with the identification of Rammelsbergite, a nickel arsenate (sub-chapter 4.1.1, p. 47).

Some of the enamel layers show micro-cracks (cf. Figure 4.16a). They either run roughly parallel to the surface or in a diagonal direction. Sometimes they continue into the base glass. The enamels analysed by Van der Snickt *et al.* show similar characteristics (Van der Snickt *et al.*, 2006). In some cases, these cracks seem to connect the gas bubbles and sometimes continue into the glass substrate (Figure 4.18).

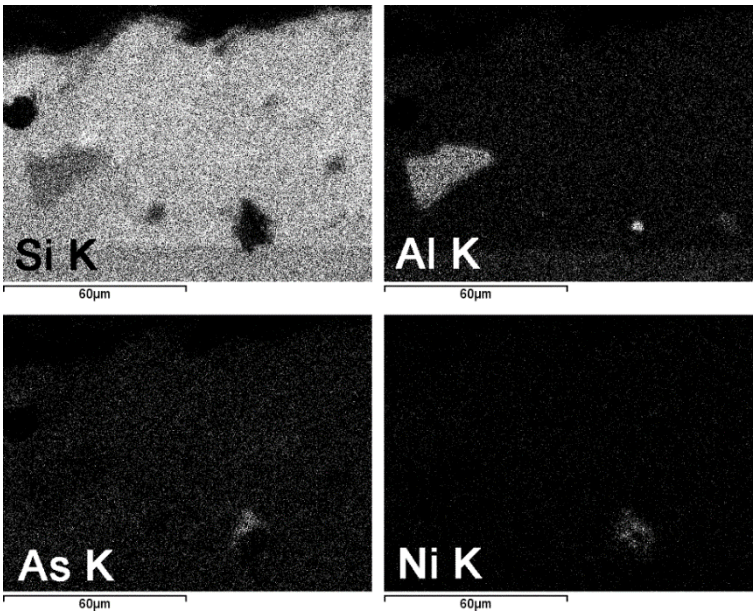


Figure 4.17 – SEM-EDS map of sample PNP12. A glassy matrix with aluminium-rich inclusions can be observed as well as an area enriched in arsenic and nickel.

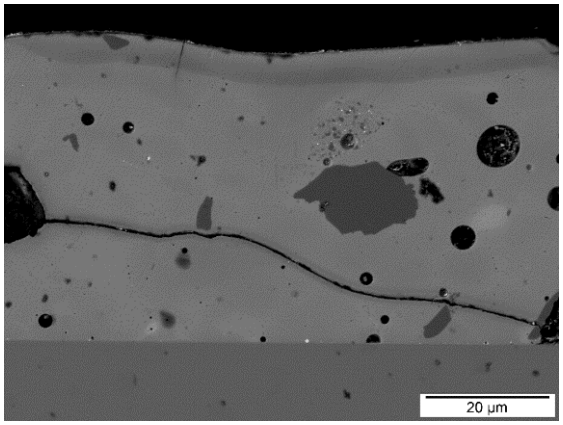


Figure 4.18 – SEM/BSE image of sample VCR02 showing air bubbles and inclusions in the blue enamel layer. The micro-crack running diagonally to the surface connects two gas bubbles.

EDS and µ-PIXE analysis show that all the blue enamels belong to the Co-As-Ni-Bi group identified by Gratuze et al. (Gratuze *et al.*, 1992, 1996) (Table V.2, AppendixV), which indicates that the cobalt ore used to produce the enamel probably came from the mining district of Schneeberg, Germany, which was exploited between the 16th and 18th centuries (Kunckel, 1752). The blue enamels of the VCR set have CoO concentrations ranging between 0.33 wt% and 3.49 wt%, and low to intermediate contents of PbO varying between 0.18 wt% and 5.1 wt%. The blue enamels from the PNP set show CoO concentrations between 2.02 wt.% and 3.2 wt.%; PbO concentrations in these samples are below the detection limit.

The contents of nickel and arsenic (as well as bismuth), which are associated with the cobalt ore, are very similar in the samples from both sets, with exception of samples VCR03 and PNP17 (Figure 4.19). However, these differences probably reflect natural variations of NiO/CoO that can occur on the cobalt ore (Gratuze *et al.*, 1992).

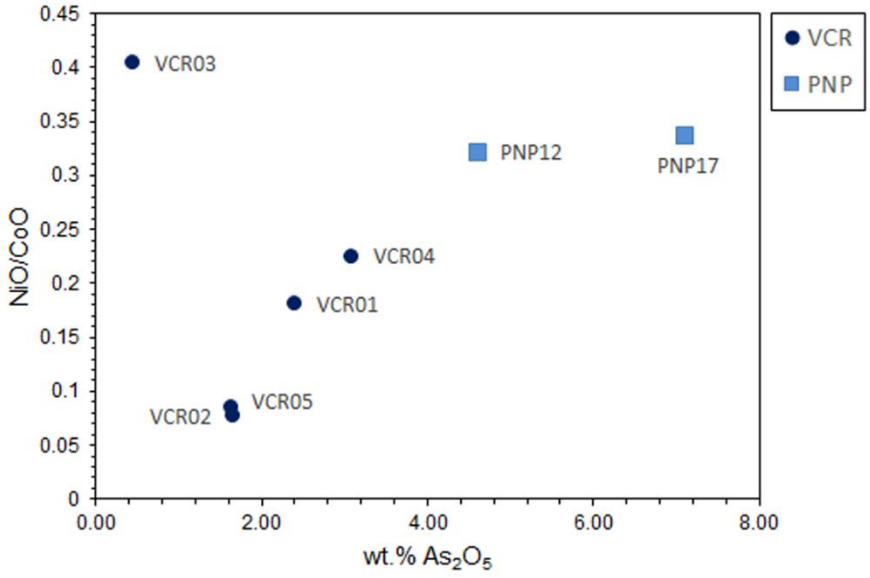


Figure 4.19 – As_2O_5 vs. NiO/CoO biplot for the blue enamel samples analysed.

The blue enamels of two samples (VCR02 and VCR05) stand out for their relatively high lead content. Lead is also related to the cobalt ore. These two enamels also have similar aluminium, titanium and iron concentrations, elements which are associated with the silica used for the production of the enamel. It seems likely that the blue enamel of these two samples was made using the same recipe. Regarding the other samples analysed, the variable composition of the enamels seems to suggest the use of slightly different enamel recipes but using cobalt ore from the same provenance as a colourant.

4.1.4. Corrosion studies on blue enamels

Corrosion of blue enamel powder samples[26]

The discoloration of smalt was already reported in a 17th century De Mayerne manuscript which associated the problem with the binder used in the paint (Boon *et al.*, 2001; Bischoff, 2002). However, recent studies have shown that the discoloration of this pigment is actually due to the leaching of potassium ions from the glass matrix to the binding medium, causing a rearrangement of the structure, specifically a change of the cobalt coordination from tetrahedral to octahedral (Boon *et al.*, 2001;

[26] The content of this sub-chapter is published in Machado, A. and Vilarigues, M. (2018) 'Blue enamel pigment – chemical and morphological characterization of its corrosion process', *Corrosion Science*. DOI: 10.1016/j.corsci.2018.05.005.

Robinet, Spring and Pagès-Camagna, 2013). Robinet et al. have shown that the Co-O distance increases in the altered pigment, affected by the Co/K ratio (Robinet *et al.*, 2011).
The previously mentioned studies focused on historical samples of smalt in easel and fresco painting. Cianchetta et al. conducted experimental studies on artificially aged samples, including smalt paint (Cianchetta *et al.*, 2012). We studied enamel applied on glass, using a sample set produced according to historical recipes which were corroded through an artificial weathering process. We analysed the results of this experimental process by various methods to characterise the corrosion mechanisms found.

The blue enamels samples were produced according to the prescriptions given by Robert Dossie in his treatise *The Handmaid to the Arts*, dated to 1758. 16 enamels were produced, eight of these used zaffer as a colouring agent while the others used smalt. The experimental procedure is described in the sub-chapter 4.1.2, pp. 53-55. The size of the particles was determined through examination of each sample under a magnifier, on this basis we selected samples to prepare the dispersions. In turn, the dispersions were examined by transmitted light optical microscopy, under plane and cross polarised light. Optical microscopy analyses to samples of the dispersions of each enamel recipe is presented in Appendix VI. The average particle size of the final enamel powder samples was 50 μm. They demonstrate a variable grain size, between approximately 1 μm and 100 μm. The grains are heterogeneous in shape, presenting a bluer colour for the samples of the enamel recipes with zaffer as colouring agent. As for the corroded enamel samples, a loss of the blue colour is noticeable. The size and shape of the grains remains heterogeneous, however we cannot assume that a change in size and shape occurred after the corrosion process.
10 enamel recipes were chosen for study out of the 16 available in Dossie's treatise: five recipes using zaffer and the equivalent five recipes using smalt. Zaffer is a mixture of SiO_2 and CoO (2:1, w/w) (Holbach, 1752), whereas smalt is a prepared blue glass (71% SiO_2, 7% CoO, 21% K_2CO_3 and 1% Al_2O_3) (Brady and Clauser, 1989). The amount of colouring agents added was of equal weight for each recipe, therefore the recipes using smalt had less cobalt in the final enamel pigment. Additionally, the enamels with smalt as a colouring agent contain alumina in their composition, which, acting as a stabilizer in the glass matrix, will have an influence on the corrosion process. Three 0.25 g replicate samples of each enamel powder were placed in 25 ml of distilled water for 2 months, without stirring, to induce corrosion. Previous studies have shown that still water, without stirring, favours the formation of crystals on the glass samples (Vilarigues & da Silva, 2009). Using distilled water without agitation can present similar results to the real weathering conditions. Inert polyethylene containers were used in order to avoid chemical reactions between the electrolyte and the container walls. Daily pH measurements were performed for a period of five days, reduced thereafter to once a week for the rest of the experimentation period. The equipment used was a Sartorius DocupH_{meter}, using an electrode with a KCl 3M solution. The electrode was calibrated with three pH solutions (4, 7, and 10) before performing the measurements; the electrode was carefully cleaned with distilled water between measurements. The

enamel powder samples, before (hereafter referred to as pristine) and after corrosion (hereafter corroded) were studied by means of a multi-analytical approach. This involved assessing its structure, both chemical and morphological, and colour by various techniques.

The corrosion mechanism was evaluated through pH measurements of the electrolyte during the experiment. The pH variation of the electrolyte is presented in Figure 4.120. The pH variation curve is in accordance with the corrosion mechanism of silicate glasses doped with metallic ions (Vilarigues and da Silva, 2009). The pH increase is very high at the beginning, followed by a slight decrease of the growth rate.

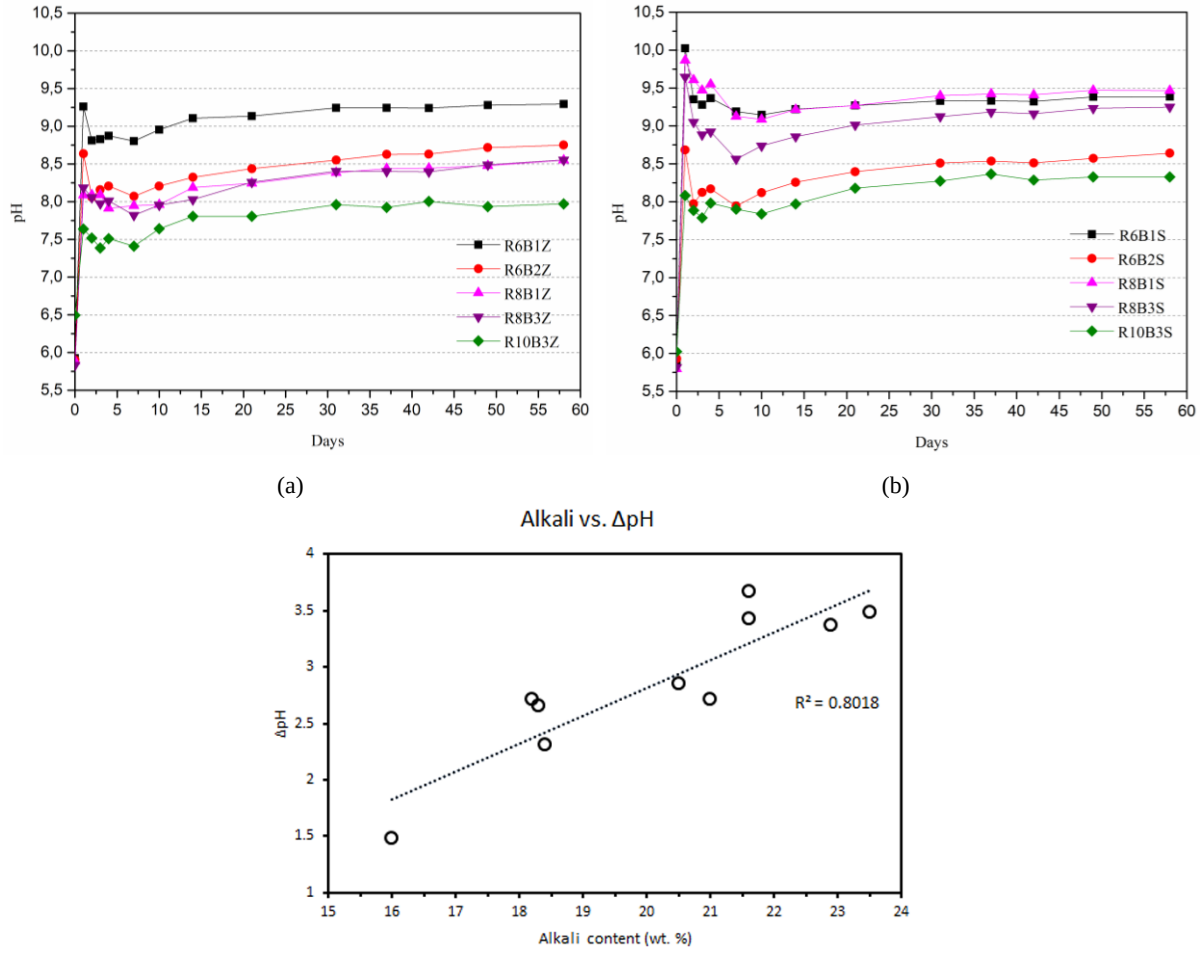


Figure 4.20 – pH variation of the electrolyte used for the corrosion of the enamel powder samples with (a) the use of zaffer and (b) the use of smalt as colouring agents. The relation between the nominal composition of the alakali and the ΔpH is presented in (c).

This decrease can be explained by the saturation of silicic acid in the solution, as the enamel samples were corroded in a static leach (Grambow, 1992). The corrosion mechanism can be explained as an initial leaching of the alkaline ions from the glass matrix to the electrolyte, allowing an ionic exchange between these ions and the hydrogen-bearing ions (H^+ and H_3O^+) of the water. The lixiviation of the alkaline ions into the water increases the pH of the electrolyte. The ionic exchange is complemented with the formation of molecular water as Si-O-Si bonds break. The pH of the electrolyte is found to have

a constant growth rate when an equilibrium of the ionic exchange is reached, leading to the formation of secondary phases, namely carbonates (Vilarigues and da Silva, 2006, 2009). In the present study, the initial pH of the electrolyte, measured without the enamel powder samples, was between 5 and 6. At the beginning of the experiment, the pH increased to 7.5-10. Previous studies have shown that glass powder samples cause such steep increases due to their high surface/electrolyte ratio (Ahmed and Youssof, 1997).

The initial increase of the pH is higher for the enamel recipes with the use of smalt as a colouring agent, an expected result since these recipes present a higher amount of alkaline ions. The final pH is, for this reason, higher than that obtained for the enamel samples with zaffer as colouring agent. Indeed, when comparing both sets of enamel powder samples (with zaffer or smalt), we can see a positive correlation between the ΔpH and the amount of alkaline: the ΔpH is higher for the enamel powder samples with a higher amount of alkaline ions in the glass composition (Figure 4.20c).

The ICP-AES characterization of the water (Table 4.11) confirms the lixiviation of the alkaline components, namely potassium. The lixiviation of K^+ ions is very heterogenous among the different recipes: it is higher (above 100 mg/l) for recipes R8B1S, R8B3S, R6B1S, R6B1Z (in this order), whereas the loss of K^+ ions for the remaining recipes is below 50 mg/l. No significant differences were identified between the enamel recipes with zaffer or smalt. There is no direct relation between the ΔpH and the overall composition of the enamel recipes, yet we can verify a positive correlation between the ΔpH and the amount of leachate alkaline ions (K^+ and Na^+), confirming an increase of alkaline in the electrolyte as a function of time.

Table 4.11 – ICP-AES results (mg/l) of the remained water used for the corrosion tests.

Sample	Al	As	B	Co	Cu	K	Na	Pb	Si
R6B1Z	0.08	nd	18.5	0.08	0.02	101.0	5.1	0.04	5.4
R6B2Z	0.15	0.41	16.3	0.01	0.01	51.9	1.5	0.05	1.9
R8B1Z	0.05	nd	nd	0.02	nd	41.3	0.85	nd	13.1
R8B3Z	0.06	nd	0.35	0.01	0.01	30.1	0.86	nd	21.5
R10B3Z	0.05	nd	nd	0.06	nd	16.2	0.48	nd	8.0
R6B1S	0.08	nd	22.4	0.02	0.01	136.6	6.3	0.07	6.2
R6B2S	0.11	0.19	10.2	nd	nd	42.9	1.2	0.05	2.4
R8B1S	0.06	nd	nd	0.04	nd	382.7	4.6	0.09	18.9
R8B3S	0.05	nd	0.60	0.07	nd	194.7	3.2	nd	27.9
R10B3S	0.04	nd	0.25	nd	nd	36.6	0.75	nd	19.4

The concentration of each electrolyte obtained by the ICP-AES technique was normalized to the concentration in the glass (by converting the elements to oxides and normalizing them to 100 %). The sodium, potassium, silicon, and boron contents of the pristine samples show a positive correlation with the given concentration in the electrolyte (Figures 4.21a and 4.21b). This indicates that their contribution to the formation of secondary phases is minimal. On the other hand, lead, aluminium, and cobalt show

no such correlation, indicating that they might contribute to the formation of secondary phases (Figure 4.21c). The measured aluminium values demonstrate that the alumina crucibles used in this experiment influenced the final composition of the enamels.

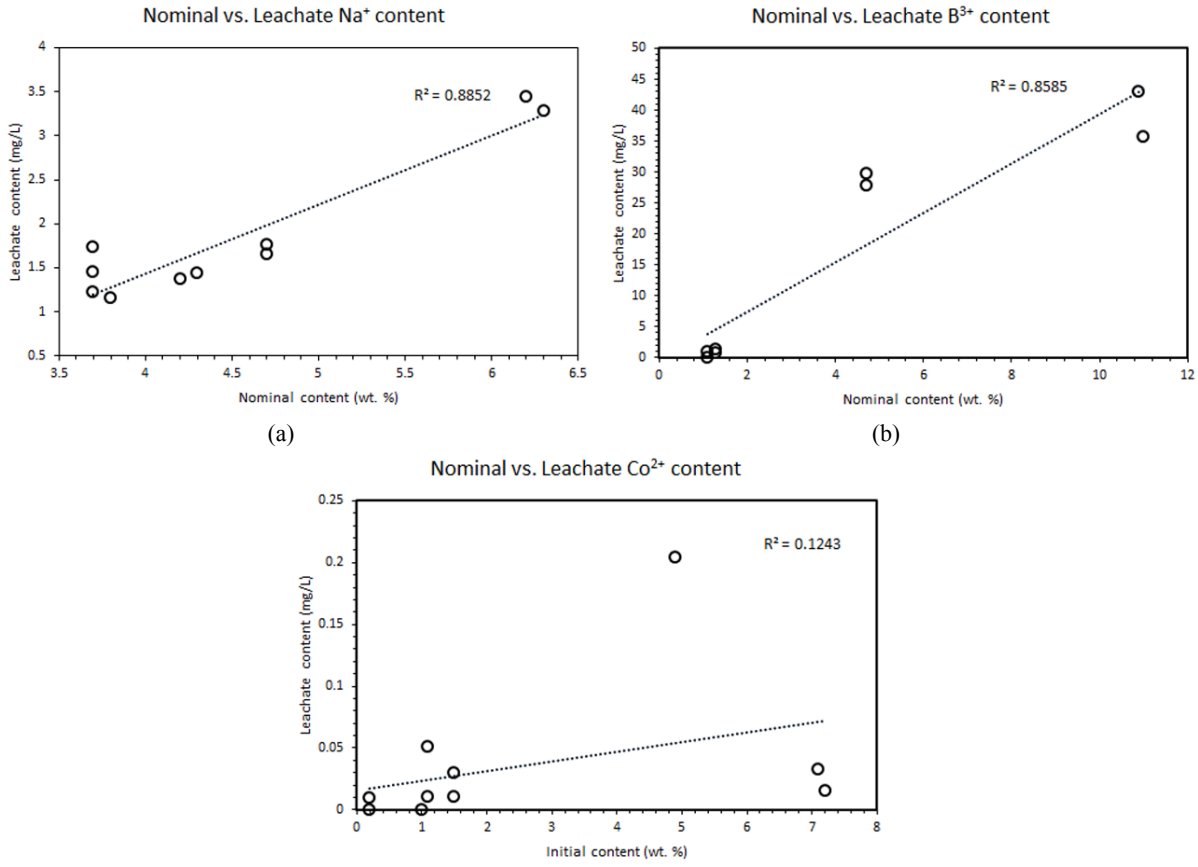


Figure 4.21 – Relation between the initial content (wt. %) and the leachate content to the electrolyte for (a) sodium ions, (b) boron ions, and (c) cobalt ions.

The visual results of the artificial corrosion process are presented in Figure 4.22. Only the samples from enamel recipes R6B1Z and R6B1S suffered a complete colour change, lightening from blue to grey. In contrast, both recipes R6B2 and R8B1Z became darker, with a negligible degree of lixiviation of cobalt ions into the electrolyte. It is possible that, with the lixiviation of the remaining ions, these two enamel samples became more "saturated" in colourant, thus darkening in colour. Meanwhile, recipe R8B1S presents a change of the blue hue in addition to a lighter colour. These visual results are attested by the measured Lab* coordinates presented in Table 4.12. The corroded samples all reveal an increase of the L* coordinate with the exception of the R6B2Z and R6B2S enamels. The b* coordinate increases for the samples with the base glass 1, i.e. R6B1Z, R8B1Z, R6B1S, and R8B1S, while the remaining samples show decreases. As for the a* coordinate, an increase is observed for all the enamel powder samples, with the exception of R8B1Z, R10B3Z and R10B3S. Figure 4.23 illustrates these results; in particular showing that the a* coordinate of enamel recipe R6B1 shifts from negative to positive, hence its dramatic change of colour when compared to the rest of the samples.

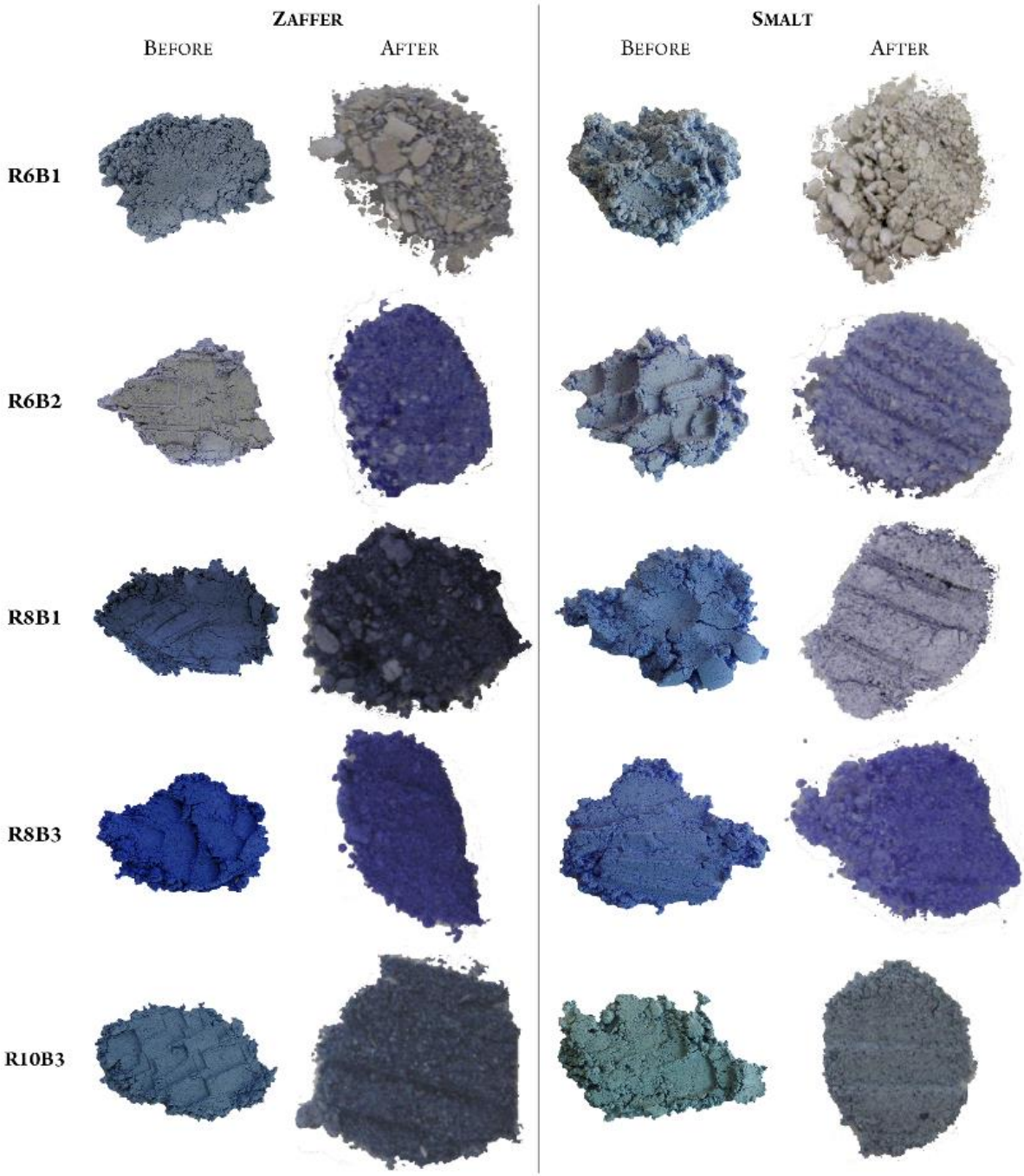
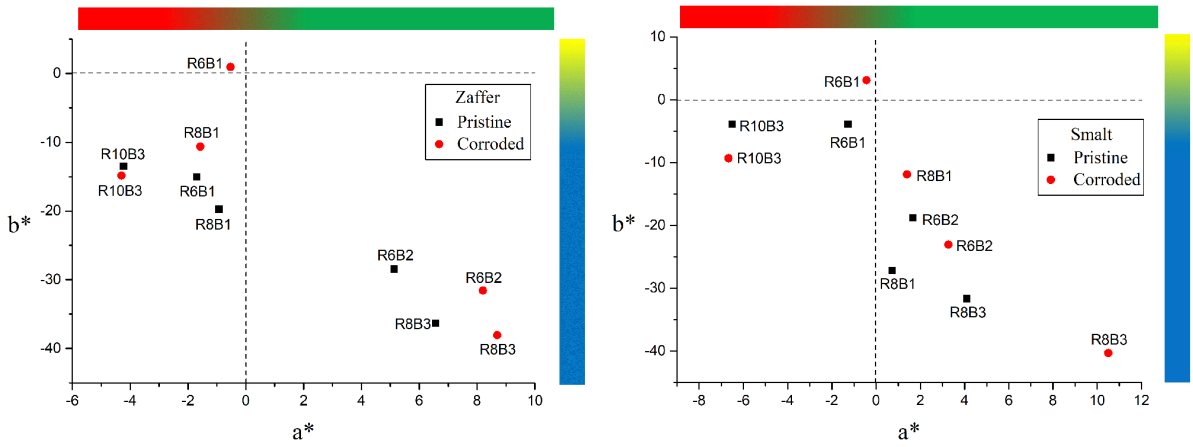


Figure 4.22 – Results of the pristine and corroded samples of the blue enamel recipes case study.

Table 4.12 – Lab* coordinates for the corroded enamel powder samples.

Recipes		Pristine			Corroded		
		L*	a*	b*	L*	a*	b*
Zaffer	R6B1	69.57	-1.7	-15.07	80.13	-0.53	0.93
	R6B2	68.7	5.13	-28.43	63.20	8.20	-31.57
	R8B1	54.4	-0.93	-19.73	58.33	-1.57	-10.63
	R8B3	53.57	6.57	-36.3	58.13	8.70	-38.07
	R10B3	59.17	-4.23	-13.53	64.53	-4.30	-14.87
Smalt	R6B1	84.27	-1.27	-3.87	90.23	-0.43	3.10
	R6B2	81.07	1.67	-18.77	78.37	3.27	-23.07
	R8B1	61.47	0.73	-27.2	76.10	1.40	-11.87
	R8B3	64.8	4.1	-31.63	57.73	10.50	-40.30
	R10B3	64.6	-6.5	-3.87	69.60	-6.67	-9.30



(a) (b)

Figure 4.23 – a* vs. b* chart for the pristine and corroded enamel powder samples, with the use of (a) zaffer, and (b) smalt as colouring agents.

The UV-Vis spectra obtained for the corroded enamel powder samples R6B1Z and R6B1S show a shift in the first band of the cobalt triplet towards lower wavelengths when compared to measurements of their pristine state (Figure 4.24). The first band is positioned around 535 nm for all the samples, a result also identified by Ceglia et al. for Na-rich glass from the post-medieval and industrial periods (Ceglia *et al.*, 2012). This indicates that the predicted lixiviation of the K^+ ions did in fact changed the chemical structure of the glass matrix and, therefore, the influence of neighbouring alkaline ions is possibly transferred to the Na^+ ions. The colour change from blue to grey in corroded samples R6B1Z and R6B1S is attested by the almost complete absence of the Co^{2+} triplet on their UV-Vis spectra. In addition to the characteristic Co^{2+} triplet, an absorption band centred at 410 nm is observed for both corroded enamel samples. This corresponds with the brighter colour displayed by these samples since white is absorbed within the 330-420 nm range (Picollo *et al.*, 2007). Enamel recipe R10B3Z shows a less pronounced Cu^{2+} absorption band, which would explain its slight colour change, as was verified by the Lab*

coordinates we obtained (cf. Table 4.12 and Figure 4.24c). The UV-Vis spectra obtained for the remaining samples are presented in Appendix VII.

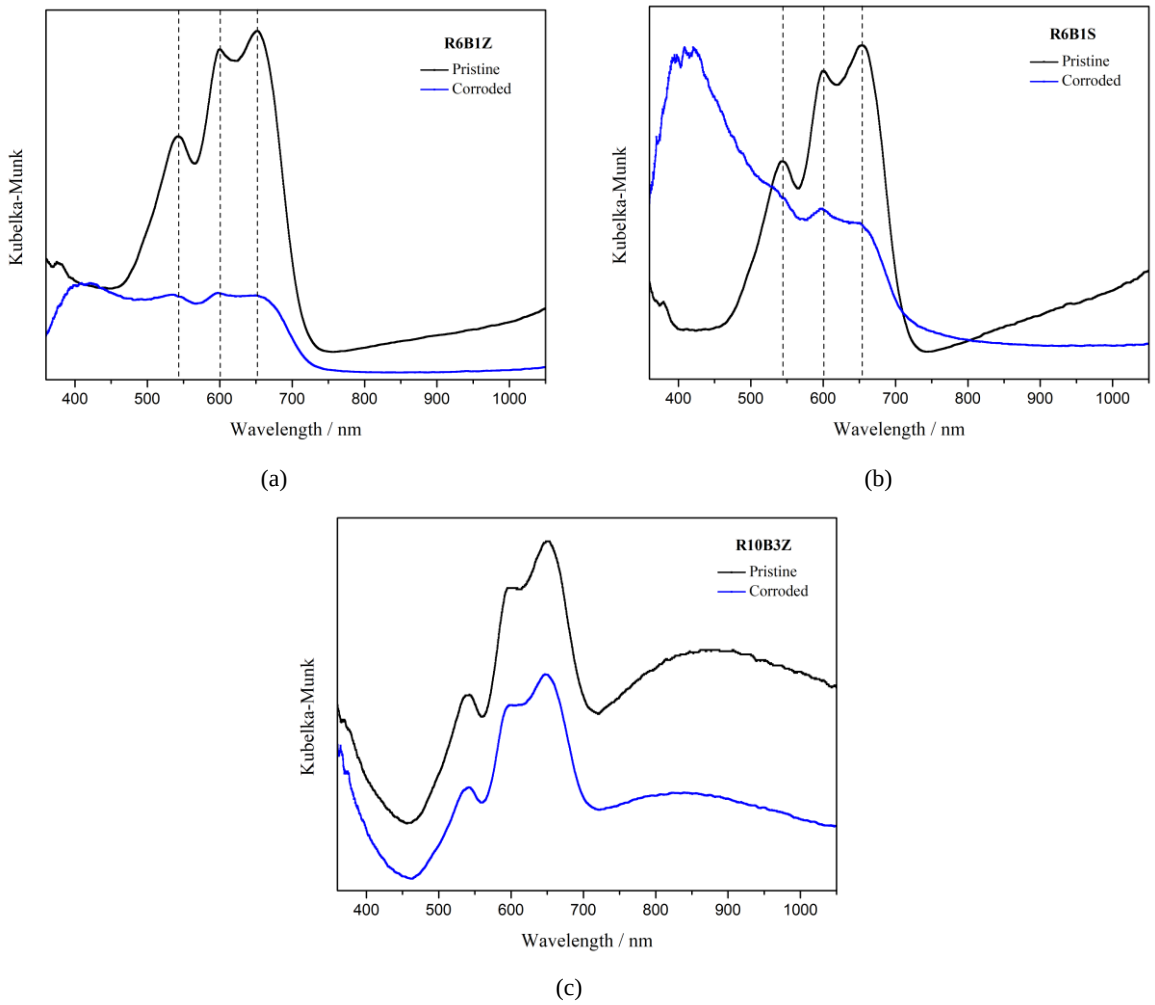


Figure 4.24 – Absorption spectra for the pristine and corroded enamel samples R6B1with (a) the use of zaffer, (b) the use of smalt as colouring agents, and (c) pristine and corroded enamel sample R10B3Z.

Further to the changes in colour already discussed, infrared spectroscopy reveals a change in the chemical structure of the enamel recipes R6B1, with both zaffer and smalt as colouring agents (Figure 4.25, and Appendix VIII for recipes R6B2, R8B1, and R8B3). The pristine enamel samples present an absorption band for the Si-bridging oxygen vibration situated between 984 cm^{-1} and 991 cm^{-1} (Vilarigues and Da Silva, 2004). The presence of cobalt oxide is shown by the absorption band situated at 469 cm^{-1}. In addition, a C-O stretching band characteristic of carbonates is present with an absorption band between 1420 cm^{-1} and 1430 cm^{-1} (Gadsden, 1975; Derrick, Stulik and Landry, 1999). The presence of a weak absorption band at 690 cm^{-1} indicates the presence of lead white cerussite ($PbCO_3$), that may have occurred already during the heating process. Following the corrosion process, the enamel samples show an O-H stretching band for OH^- bonds between 3420 cm^{-1} and 3430 cm^{-1}. The loss of the alkaline ions, mainly of K^+ ions during the experiment had affected the glass structure: the absorption band for

the Si-bridging oxygen vibration seen previously was absent, and a weak absorption band centred around 890 cm^{-1} related to the $Si\text{-}O^-$ vibration had become visible (Vilarigues and da Silva, 2009).

In addition, a series of infrared spectroscopy measurements marked changes to the chemical structure of these R6B1 samples, detailed as follows. A sharp absorption band between 1025 cm^{-1} and 1030 cm^{-1} corresponding to the Si-O-Si vibration (Vilarigues and da Silva, 2006). A weak absorption band around 3530 cm^{-1}, characteristic of a hydrated carbonate – in this particular case hydrocerussite ($PbCO_3 \cdot Pb(OH_2)$). A sharp absorption band at around 680 cm^{-1} confirms the presence of lead carbonate cerussite. An absorption band at around 1640 cm^{-1}, related to the presence of hydrated cobalt oxide (CoO(OH)) (Gadsden, 1975; Derrick, Stulik and Landry, 1999). The C-O stretching band of CO_3^{2-} had become sharper and deviated to a position around 1400 cm^{-1}. Significantly, the formation of hydrated lead white – a white pigment – suggests that the Pb^{2+} ions have an important role in the change of colour observed for the corroded enamel sample R6B1. The presence of the absorption band centred at 410 nm in the UV-Vis spectra confirms this hypothesis (cf. Figure 24).

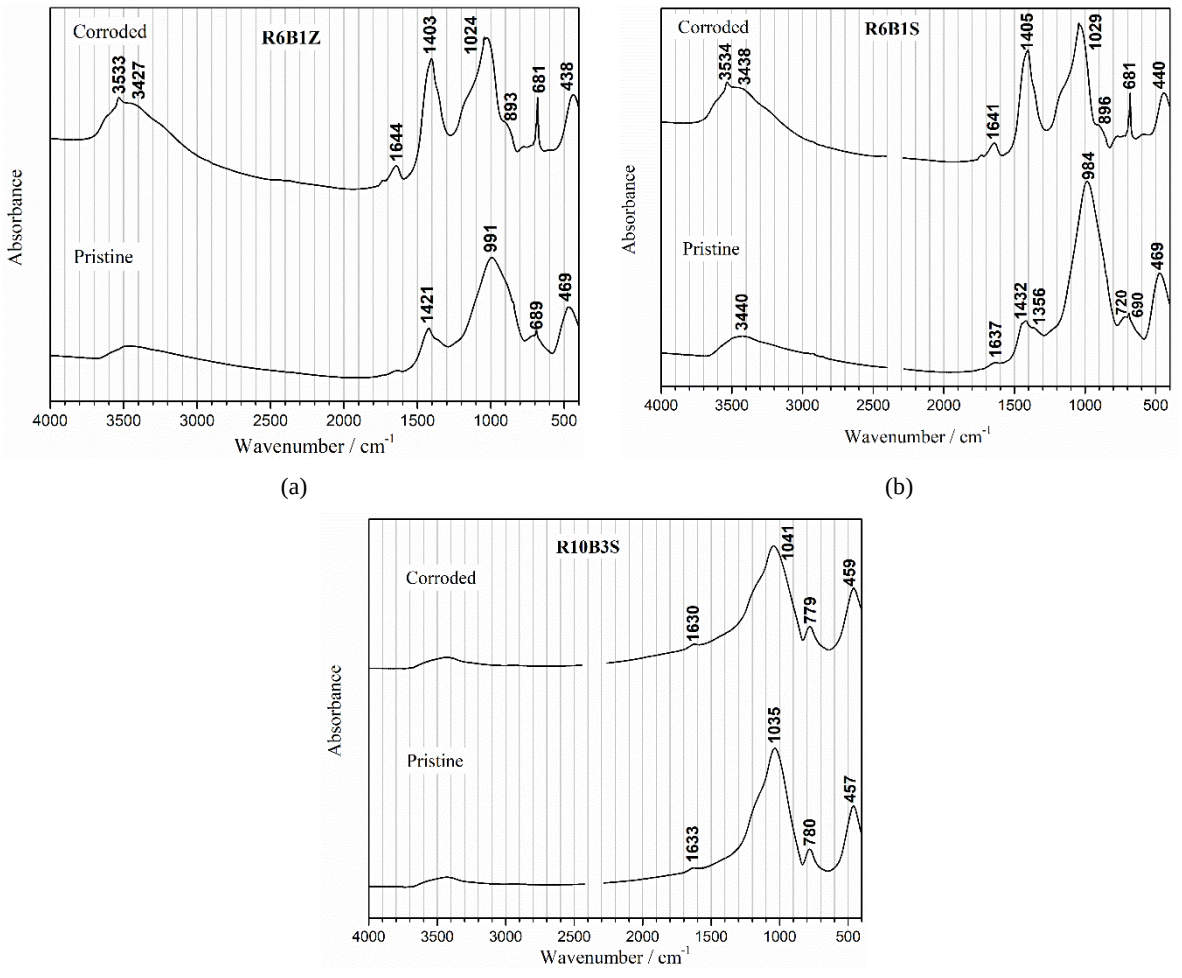


Figure 4.25 – Infrared spectra of the enamel samples R6B1, (a) with the use of zaffer, (b) the the use of smalt as colouring agents, and (c) enamel sample R10B3S, before and after corrosion.

As for the remaining enamel samples, no significant changes occurred after the corrosion process. Enamel recipes R10 (Figure 25c) present a sharp Si-O$^-$ stretching band around 1040 cm^{-1}. The presence of a weak band at 779 cm^{-1} may indicate the presence of cuprite (Cu_2O). The absorption band between 459 and 463 cm^{-1} is characteristic of the cobalt oxide (Gadsden, 1975; Derrick, Stulik and Landry, 1999).

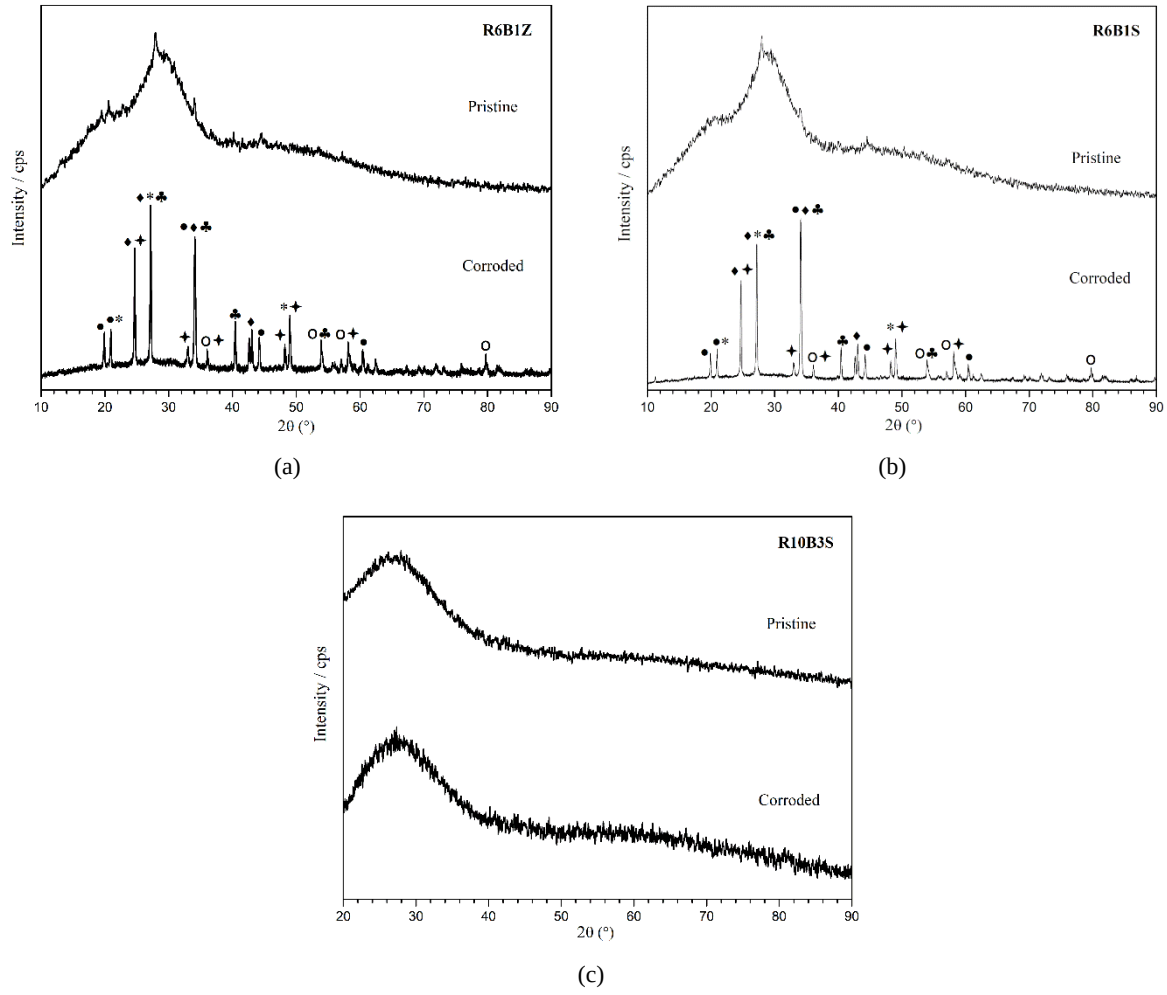
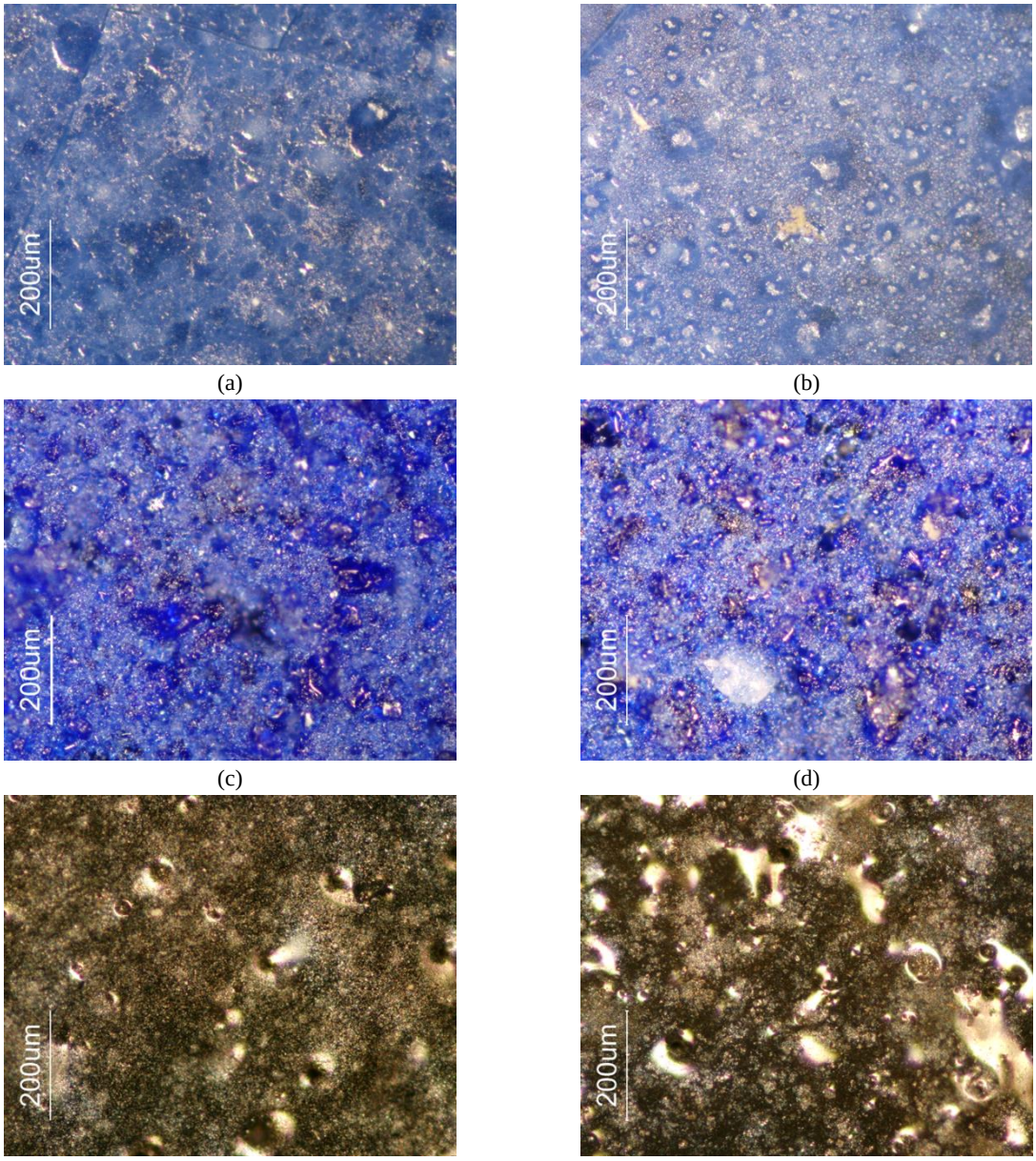


Figure 4.26 - XRD patterns for the corroded enamel recipes R6B1, (a) with the use of zaffer and (b) with the use of smalt as colouring agents, and (c) enamel sample R10B3S, before and after corrosion.
• – Co_3O_4 ; ♦ – $KAlSiO_4$; ∗ - SiO_2 ; o – $CoAl_2O_4$; ✦ – cerussite $PbCO_3$; ♣ – hydrocerussite $PbCO_3{\cdot}Pb(OH_2)$.

X-ray diffraction confirmed the information given by infrared analysis. This analysis showed that significant changes had occurred in the chemical structure of the corroded enamel samples, mainly for enamel recipes R6B1Z and R6B1S (Figure 4.26). R6B2Z, R8B1Z, R6B2S, and R8B1S also presented crystalline phases; however, we do not see a complete structural change as in samples R6B1Z and R6B1S (Appendix IX). The enamel recipes R8B3 and R10B3 included both colouring agents, they do not present any crystalline phases after corrosion, showing instead an amorphous structure common to a cobalt glass (Figure 4.26c) (Jonynaite *et al.*, 2009). The following crystalline phases were identified: cobalt oxide (Co_3O_4), quartz (SiO_2), kalsilite ($KAlSiO_4$), cobalt aluminate ($CoAl_2O_4$), cerussite ($PbCO_3$) and hydrocerussite $PbCO_3{\cdot}Pb(OH_2)$. As described in the ICP-AES results, no correlation between lead,

aluminium, and cobalt contents of the pristine samples and the given concentration in the electrolyte was found (cf. Figure 4.21c). This result agrees with the information provided by FTIR and XRD analyses, thus confirming the formation of hydrated lead white, and Co^{2+}/Co^{3+} spinels as secondary phases. The leaching of the alkaline ions along with the ionic exchange between these ions and the hydrogen-bearing ions (H^+ and H_3O^+), promoted a rearrangement of the glass structure, with the formation of crystals such as Co^{2+}/Co^{3+} spinels. In addition, hydrated lead carbonate was formed. It was possible to determine the presence (even if discrete) of lead carbonate cerussite before the corrosion process took place, indicating that this compound was already formed during the heating process. This result was also verified by the infrared analysis.



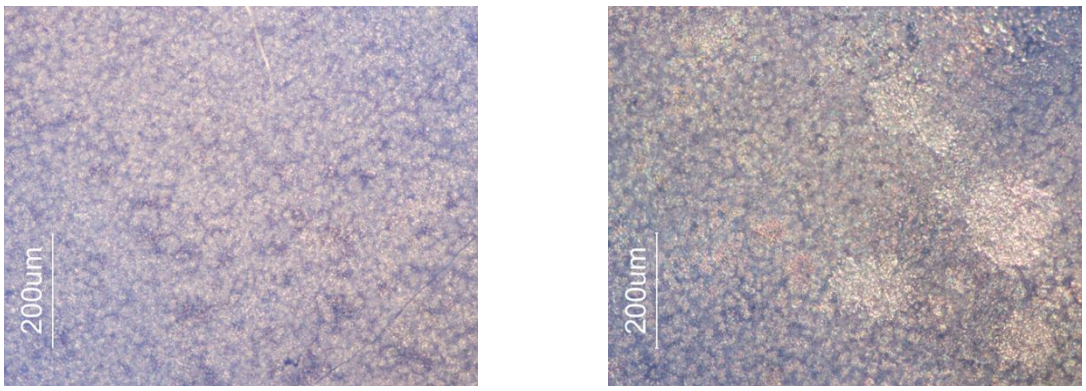
(a) (b) (c) (d) (e) (f)

Figure 4.27 - Optical microscope images of three paint samples: R6B1Z, before (a), and after corrosion (b), R8B3Z, before (c), and after corrosion (d), and R10B3S, before (e), and after corrosion (f).

Corrosion of blue enamel paint samples

The corrosion of the blue enamel paint samples considered the contribution of the relative humidity. The selected samples were placed in a closed desiccator for a period of 12 months, maintaining a relative humidity around 80 %.

Optical microscopy imaging allowed to detect differences at the surface of the paint samples. Generally, the surface of the painted samples became duller, a result of the high relative humidity to which they were subjected (Figure 4.27, and Appendix X). In some cases, the appearance of small white areas at the surface are visible, as is the case of paint sample R6B2Z (Figure 4.28). Lead carbonate was identified through Raman spectroscopy, with the presence of a peak at 1057 cm^{-1} (Burgio, Clark and Firth, 2001), which can explain this phenomenon. In addition, cobalt silicate (Co_2SiO_4) was identified with the typical band centred around 820 cm^{-1} (de Waal, 2009) (Figure 4.29). Furthermore, micro-crystals were identified at the surface of the enamel paint layers R6B2, determined by EDS analysis as Na-rich (Figure 4.30).



(a) (b)

Figure 4.28 – Optical microscope images of the paint sample R6B2Z, (a) before and (b) after corrosion. The presence of small white areas at the surface of the corroded paint sample is visible.

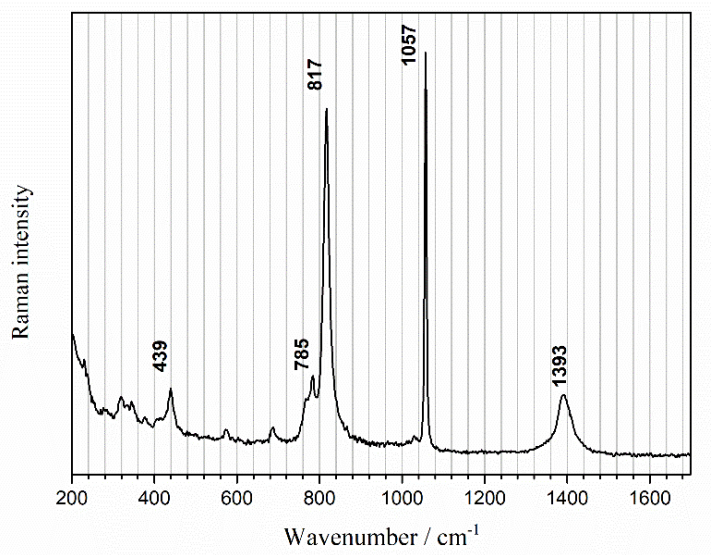
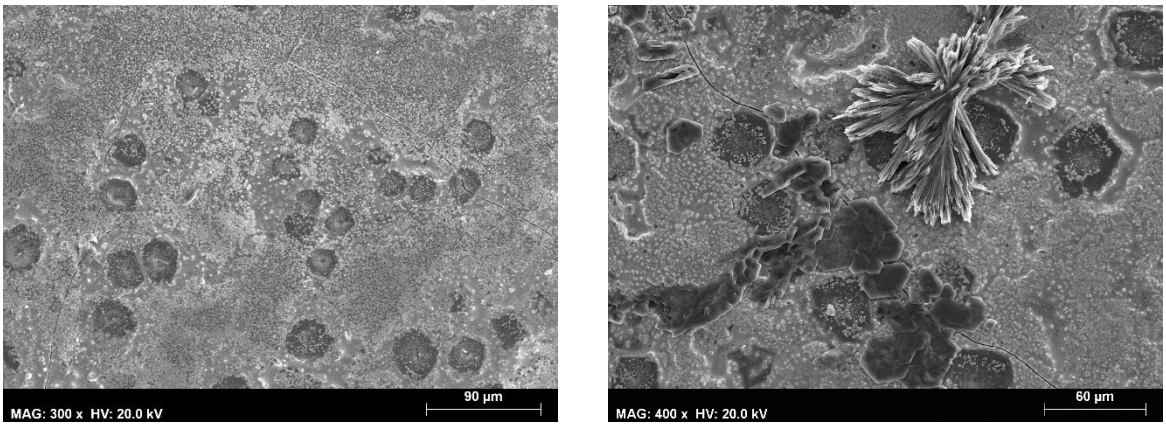


Figure 4.29 – Raman spectrum of a lead carbonate present on the enamel paint R6B2Z.



(a) (b)

Figure 4.30 – SEM-EDS images of corroded paint sample R6B2S, with the presence of micro-crystals at the surface (b).

Colorimetric measurements using the Lab* system for the enamel samples after the corrosion process (Table 4.13) revealed for most of the enamel samples, an increase of the L* coordinate, which is in agreement with the result shown by optical microscopy imaging. The b* coordinate increases for the majority of the enamel paints with the use of zaffer, and for the enamels R6B2S and R10B3S. As for the a* coordinate, enamel paints R6B1Z, R6B2Z, R6B3Z, R6B1S and R6B2S revealed lower values. Enamel paint R8B1S is the only sample which a* coordinate increased from a negative value to a positive value.

Table 4.13 – Lab* coordinates for enamel paint samples, before and after corrosion.

	Recipe	**Pristine**			**Corroded**		
		L*	**a***	**b***	**L***	**a***	**b***
Zaffer	R6B1	21.5	14.9	-41.27	27.37	9.13	-36.13
	R6B2	43.93	10.7	-38.77	43.53	6.33	-33.80
	R8B1	23.17	31.6	-61.1	15.70	34.13	-57.30
	R8B3	19.17	24.93	-43.87	22.63	14.13	-34.17
	R10B3	22.53	-0.27	-1.03	18.03	-0.87	-0.40
Smalt	R6B1	25.77	-0.6	-14.1	36.33	-0.43	-18.17
	R6B2	47.02	5.43	-32.53	54.47	1.03	-25.53
	R8B1	24.13	-3.03	-10.83	30.83	1.63	-33.47
	R8B3	26.6	0.03	-17.93	28.47	7.43	-38.07
	R10B3	17.77	-3	-5.47	21.63	0.37	-2.60

For enamel paint samples R6 and R8, with the use of zaffer and smalt as colouring agents, no major changes were detectable (Appendix XI). On the other hand, for enamel recipes R10B3 with the use of zaffer and smalt, the absorption bands of the Co^{2+} triplet and the one from Cu^{2+} become difficult to observe (Figure 4.31). Since no alterations on the chemical structure were detected, we can assume this alteration is related to the colour alteration at the surface of the paint sample, visible by measurement of Lab*.

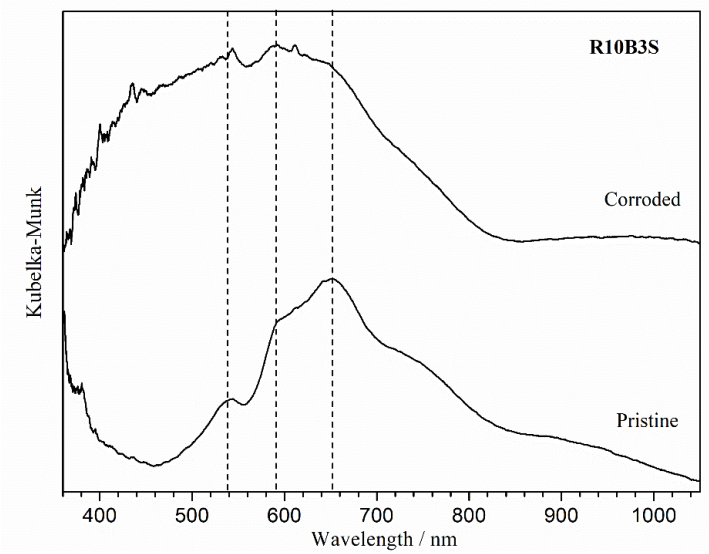


Figure 4.31 - Absorption spectra for enamel paint sample R10B3S, before and after corrosion.

4.2. Sanguine Red

4.2.1. The recipes

The use of iron red for painting is known since ancient times. Its application extended through various substrates, including stained glass, where many times translucent sanguine was used for carnations. Its application in stained glass began probably in the second half of the 15th century (Caen, 2009). Historical recipes dated to between the 17th and the 18th centuries show that sanguine red was obtained from hematite (α-Fe_2O_3), giving various tones from red to brown, and treated to be applied as a more transparent or opaque colour.

Antonio Neri in his treatise *L'Arte Vetraria* writes about how to make *Crocus Martis* (the alchemical name for red iron oxide), saying "this way causes the glass to appear a rather bright blood red" (Engle 2003, vol. I, p. 34). Neri presents 4 recipes on how to prepare this pigment. One of the recipes involves mixing iron with sulfur and further calcination of the mixture (chapter 16, *A fare il Croco di ferro, altrimenti detto di Marte per i colori del vetro*). The other three recipes are prepared from a corrosion process with acetic acid and nitric acid (chapter 17, *A fare Croco di Marte in altra maniera*, chapter 18, *Altro modo di fare il Croco di Marte*, chapter 19, *A fare il Croco di Marte in altra maniera*).

Kunckel in his treatise *Ars Vitraria Experimentalis* presents three recipes on how to prepare sanguine, the co-called *couvertes rouges*. Unlike the recipes given by Neri, the recipes given by Kunckel prescribe the use of antimony and vitriol (sulphuric acid), and one of the recipes includes the addition of glass.

Pierre Le Viel presents various translations and recipes for the production and application of this pigment. In addition, original recipes for the preparation of sanguine are described. To all the recipes *rocaille* (75 wt.% PbO + 25 wt.% SiO_2) is added, along with powdered gum arabic, lead, and in one case bismuth (Schalm et al., 1996). The list of the recipes is presented in Table 4.14.

Table 4.14 - List of the sanguine red recipes from historic treatises dated to between the 17th and the 18th centuries.

		Iron filings	*Crocus Martins / Saffran de Mars*	Sanguine	*Rocaille*	Glass	Lead	Antimony	Bismuth	Sulphur	*Caput mortuum*[27]	Gum arabic	Vinegar	*Acqua forte*[28]	Vitriol
L'Arte Vetraria Antonio Neri (1612)	1	X								X					
	2	X											X		
	3	X												X	
	4	X												X	
Ars Vitraria experimentalis Johann Kunckel (1679) In: Holbach, L'Art de la Verrerie (1752)	1	X					X	X							
	2		X				X	X							
	3		X			X					X				X
Des Principe de L'Architecture, de la Sculpture, de la Peinture (1676) André Félibien		X	X		X		X					X			
De l'Art de la verrerie Haudicquer de Blancourt (1697)		X	X		X		X					X			
L'Art de la peinture sur verre et de vitrerie (1774) Pierre Le Vieil	1	X		X	X		X					X			
	2	X	X	X	X		X					X			
	3	X		X	X		X		X			X			

[27] *Caput mortuum* (dead's head) is the alchemical name for an iron-based pigment of purple colour, obtained from hematite.
[28] Nitric acid.

This painting technique presents conservation issues that can be related to the application method, rather than with the composition of the paint (unlike the enamels, where we verify that the composition does affect its conservation state in the future). In order to address this problem, the reproduction of the sanguine recipes was performed considering the application of the paint with different binders and the firing of the paint at different temperatures, and with different heating rates.

4.2.2. The reproductions[29]

Four recipes were reproduced according to with the information given by the following treatises (Table 4.15):

Table 4.15 – The recipes for sanguine red paint technique reproduced in this study.

L'Arte Vetraria Antonio Neri 1612	chapter 17, *A fare Croco di Marte in altra maniera*	**R1**
	chapter 18, *Altro modo di fare il Croco di Marte*	**R2**
Ars Vitraria Experimentalis Kunckel 1679	*chapter 51– Belle couverte rouge*	**R4**
L'Art de la Peinture sur Verre et de Vitrerie Pierre Le Vieil 1774	*chapter 5 - Carnation des frères Maurice & Antoine*	**R3**

For the preparation of the recipes 1 and 2, low carbon steel filings (<2 %) were used. The choice of this material is related with the close resemblance with iron cast used in that period. The modern metal alloys are produced together with other components with the aim to enhance the properties of the material. For both recipes, the carbon steel filings were placed on Petri dishes and soaked with the acid prescribed for each recipe (acetic acid for recipe R1, and nitric acid for recipe R2). Once dried, the final product was grinded, and if needed the process was repeated. Overall, both recipes were soaked in acid and grinded 5 times each (hereafter 5 times in acid). However, both pigments were used to paint after soaked and grinded only two times with the respective acids (hereafter 2 times in acid).

The iron filings oxidise in contact with the acetic acid resulting in the formation of iron (II), according to the following chemical reaction (Weber *et al.*, 2011):

$$\mathrm{Fe} + 2\mathrm{CH_3COOH} \rightarrow \mathrm{Fe}(C_2H_3O_2)_2 + \mathrm{H_2} \quad (1)$$

As for the corrosion process with nitric acid, ferric oxide is formed, according to the following chemical reaction (Fujihara, 1926):

[29] The first reproductions of the recipes were made in 2014, within a project by Fernanda Carvalho for the master course of History of Art Technology and Materials.

$$2\mathrm{Fe} + 2HNO_3 \rightarrow Fe_2O_3 + H_2O + 2NO \quad (2)$$

Recipe 3 was reproduced in line with the description given in the treatise. The components were mixed, with exception of the sanguine (Fe_2O_3), which was mixed in the end. The mixture was placed in a glass container, filled with water just enough to cover the recipe. The container was left for two days next to a window, to be exposed to sunlight. In the end, the final dried product was scratched and stored.

Recipe 4 was prepared as the prescriptions given. Iron rust was used, thus grinded mechanically.

To prepare the paint, different binders were used: a mixture of gum arabic with water, and a mixture of lavender oil and distilled turpentine. The application of the paint on the glass was made with a spatula and with a brush. To fire the paint samples, two parameters were considered: the firing temperature and the annealing rate. The paint samples were fired at 680 ºC and 700 ºC, with three different annealing rates of 5 ºC/min, 2 ºC/min, and 1 ºC/min.

The selected methodology used for the reproduction of the recipes is presented in Figure 4.32.

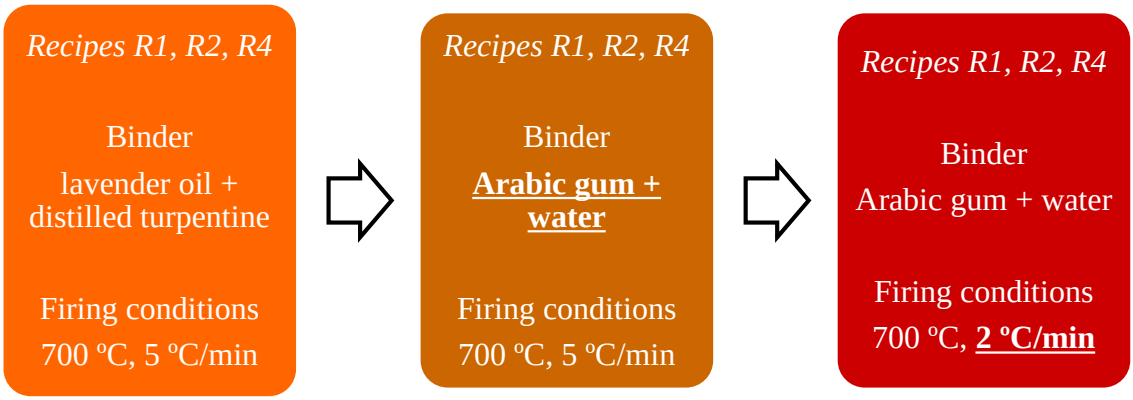


Figure 4.32 – Schematic representation of the step-by-step for the production of the sanguine red paint samples. The parameters which were shifted from one experiment to another are underlined.

The first set of painting samples was performed using a mixture of lavender oil and distilled turpentine as a binder; the samples were fired at 700 ºC, with a heating rate of 5 ºC / min. This test was performed for recipes 1, 2, and 4. The final results were not satisfactory for the recipes 1 and 2. The paint did not adhere to the surface and was easily detached just by touching the paint. Recipe 4 presented good results in terms of the adhesion of the paint, however, did not present the colour desired, resulting on a yellow paint. As a first approach the binder chosen proofs to be important to the outcome of the paint.

Pierre Le Vieil in his treatise *L'Art de la Peinture sur Verre et de Vitrerie* indicates that the application of a "watered gum arabic" is necessary to paint on glass (Vieil 1774, p. 195). In the case

of recipe 4, powdered glass and lead are part of the composition, and for this reason, the adhesion to the base glass was achieved, regardless of the binder used.

The second set of paint samples was made, with a mixture of gum arabic and water as a binder. The paint samples were also fired at 700 ºC, with a heating rate of 5 ºC / min. For all the recipes the final paint adheres to the base glass, however, it could still be removed from the surface, but to a smaller degree when compared with the previous tests.

Without changing both binding agent and firing temperature, a third test was made, changing the heating rate from 5 ºC / min to 2 ºC / min. The final result was thus optimized, presenting a good adhesion, and in addition, the paint was not removed from the surface.

With these results in mind, it was decided to maintain the heating rate of 2 ºC / min and the mixture of gum arabic and water as a binding agent. A fourth test was performed with sanguine recipe R2 to test the firing temperature, decreasing from 700 ºC to 680 ºC. This is the temperature limit prescribed by the Debitus company for the *Rouge Jean Cousin* carnation paint.

Table 4.16 – Final results for sanguine powder and paint, at 680 ºC and 700 ºC.

	Powder	Paint	
		680 ºC	700 ºC
R1			
R2			
R4			

Recipes R1, R2 and R4

Table 4.16 presents representative results of the reproductions, for both powder and paint samples. The discussion of the results will be centred on the three recipes for the powder pigment, whereas the discussion on the paint samples will be centred in sanguine recipe R2.

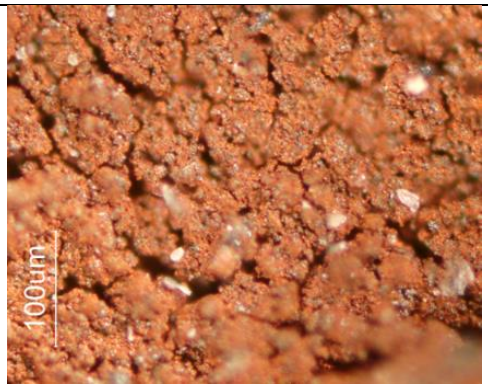
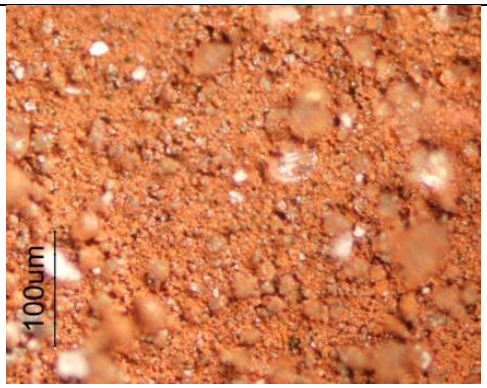
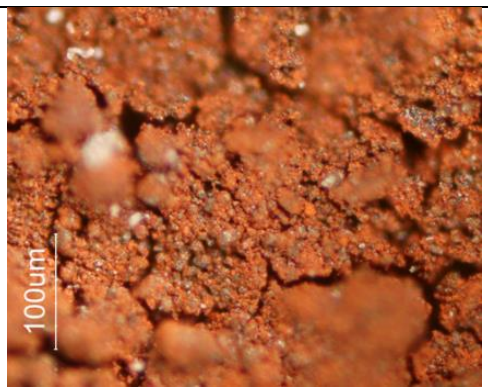
Recipe 1 resulted in a powder of reddish-brown colour. There were no relevant differences in the colour obtained after 2 and 5 times in acid. The colour obtained for the sanguine paint changed from

the brownish colour to a more reddish hue. For recipe 2 the final colour obtained for the pigment powder was brighter than the one for recipe 1, suggesting that the acid employed does affect the final colour of the pigment. After firing the paint is possible to verify that the result for recipe 2 resembles more with the final colour desired, an information already provided by Kunckel when the author specifies that the obtained from *acqua fortis* (nitric acid) is more beautiful (Holbach 1752, p. 74). Since nitric acid is a strong oxidising agent, the corrosion process resulted on a more orange colour, which after firing the paint gave room to a more homogenous and reddish hue. However, it is not similar to the red carnation colour that we see on historic sanguine red paint. There is no relevant difference between the colour obtained at 680 ºC and 700 ºC.

The colour obtained for recipe 4 was the least satisfactory of the four recipes. The powder presents a yellow hue, which did not change after firing the paint.

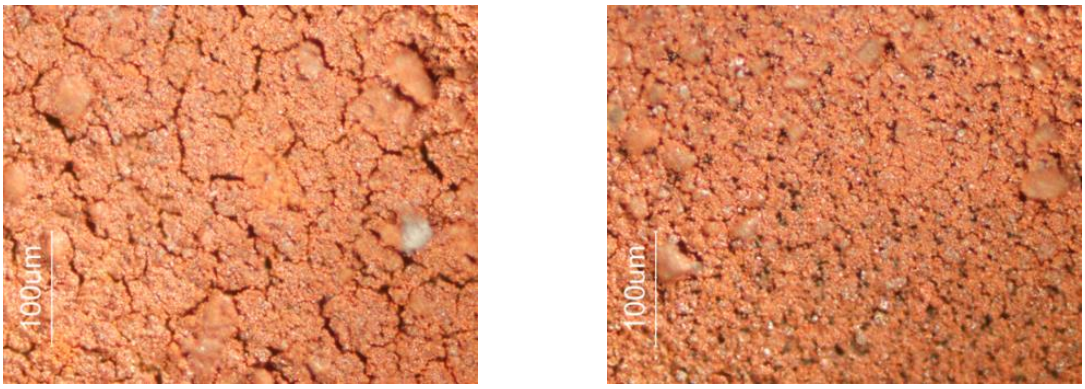
When it comes to the type of application, it was concluded that the use of a brush renders a better effect, giving a more homogeneous layer. This result is verified by optical microscopy imaging, where we can see that using a spatula the paint presents more craquelure when compared with the result obtained with a brush (Table 4.17).

Table 4.17 - Optical microscopy images of sanguine red paint recipe R2, at 700 ºC, 5 ºC / min. A mixture of lavender oil and distilled turpentine was used as a binder.

	Spatula	**Brush**
2x in acid		
5x in acid		

In addition, we can see that there are not any differences in terms of the colour obtained between the pigment achieved with two or five times in acid. By testing two different firing temperatures of

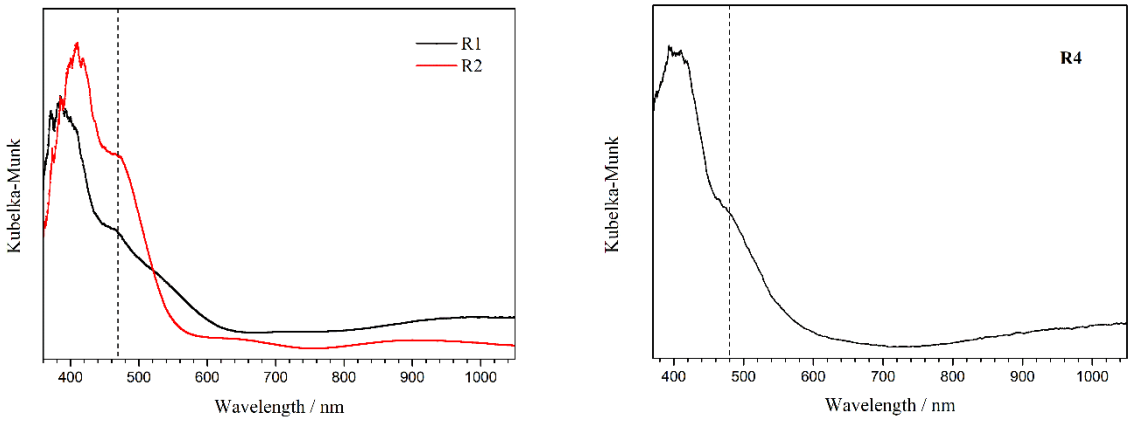
680 ºC and 700 ºC, differences can be seen on the evenness of the paint layer. Though it is a difference of 20 ºC, we can perceive that the paint sample fired at 700 ºC presents a more homogeneous layer (Figure 4.33).



(a) (b)

Figure 4.33 – Optical microscopy images of sanguine red paint recipe R2, with the use of a mixture of gum arabic and water as a binding agent, fired at (a) 680 ºC, and (b) 700 ºC. The samples were painted with a brush.

Fe^{2+} and Fe^{3+} were identified in the three powder samples. In the case of recipes R1 and R2, the spectra (Figure 4.34a) indicate the presence of ionic species formed during the corrosion of the iron filings, such as $FeOH^{2+}$, and $Fe(OH)_2^{+}$ (Schalm, 2000). Recipes R1, R2, and R4 present an absorption band centred between 469 nm (R1), 473 nm (R2), and 480 nm (R4) and a week broad band around 1000 nm (R1), 900 nm (R2), and 998 (R4). In addition, recipe R2 presents a week broad band centred on 646 nm (Figure 4.34). Infrared spectroscopy analysis of powder samples R1, R2, and R4 was also undertaken (Figure 4.35).



(a) (b)

Figure 4.34 – Absorption spectra of the powder samples of (a) recipes R1 and R2, and (b) recipe R4.

For recipe R1, the infrared spectra of the pigment after 2x and 5x in acid presented similar results. Goethite (α-FeOOH) and lepidocrocite (γ-FeO(OH)) were identified for recipes R1 and R2, with the

presence of stretching and bending vibrations of the hydroxyl groups characteristic of both pigments. The presence of stretching and bending vibrations of acetate and nitrate groups was also identified (Table XII.1, Appendix XII) (Derrick, Stulik and Landry, 1999; Schwertmann and R. M. Cornell, 2000; Helwig, 2007; Goebbert *et al.*, 2009). Regarding recipe R4, antimony pentoxide (Sb_2O_5) was identified with a week band centred at 953 cm^{-1}. Bindheimite ($Pb_2Sb_2O_7$) was likewise identified, with the presence of a strong band centred at 726 cm^{-1}. XRD analysis confirmed the information provided by the infrared spectra (Figure 4.36). In addition of antimony pentoxide and bindheimite, hematite (α-Fe_2O_3) and minium (Pb_3O_4) were also identified for recipe R4 (Gadsden, 1975; Downs *et al.*, 2017).

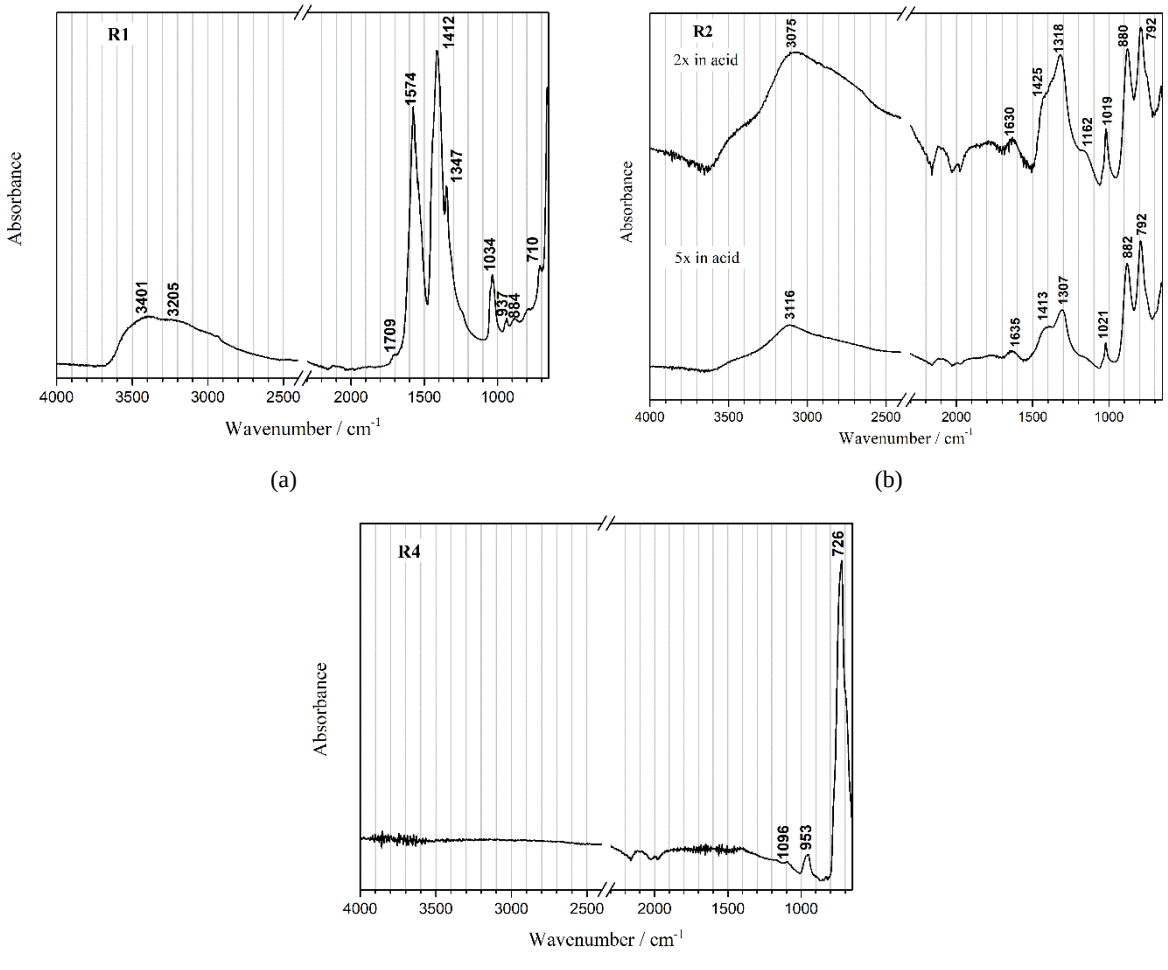
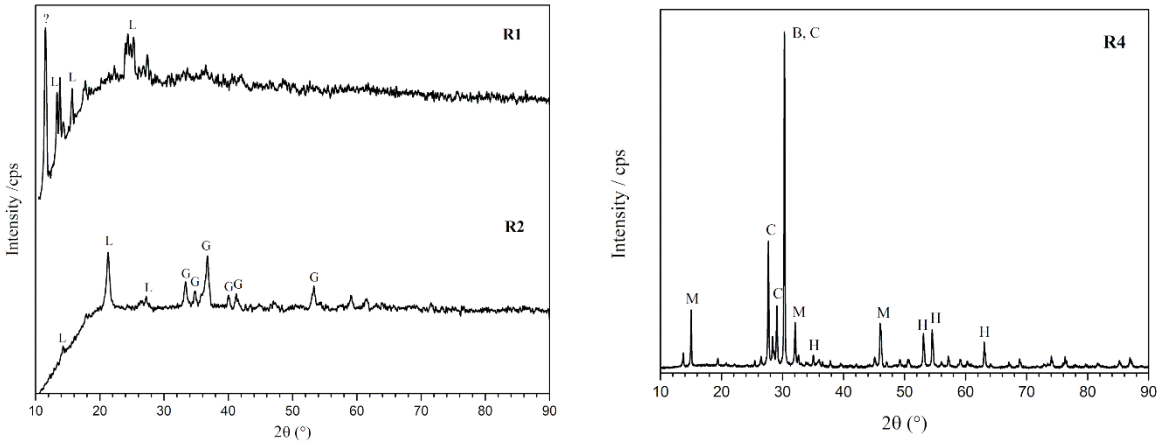


Figure 4.35 – Infrared spectra of the powder samples of (a) recipe R1, (b) recipe R2, and (c) recipe R4.

With respect to the painting sample R2, goethite and lepidocrocite were converted into hematite, identified by its characteristic Raman assignment (Figure 4.36, and Table XII.2, Appendix XII) (Cornell & Schwertmann 2003, p.147; Legodi & de Waal 2007; Legodi 2008). When comparing the powder with the paint sample of recipe R2, fired at 700 ºC, we can attest the transformation of iron hydroxides to iron oxide hematite. This is due to the heating process of the paint, forming

insoluble iron particles. According to the spectrum of the paint, all the light is absorbed up to ca. 590 nm, indicating that only the red colour is reflected. Charge transfers between Fe^{3+} and O^{2-} ions occur in this region, whereas the broad band centred on 855 nm is related to spin-forbidden ligand field transitions. The size of the iron particles was not calculated, however according to the literature a diameter between 0.1 and 1.0 µm is predicted (Schalm, 2000) (Figure 4.38).



(a) (b)

Figure 4.36 – XRD diffractograms for powder samples of (a) recipes R1 and R2, and (b) R4.
L – lepidocrocite γ-FeO(OH); G – goethite α-FeOOH; H – hematite α-Fe_2O_3; M – minium Pb_3O_4; C – cervantite Sb_2O_4; B – bindheimite $Pb_2Sb_2O_7$.

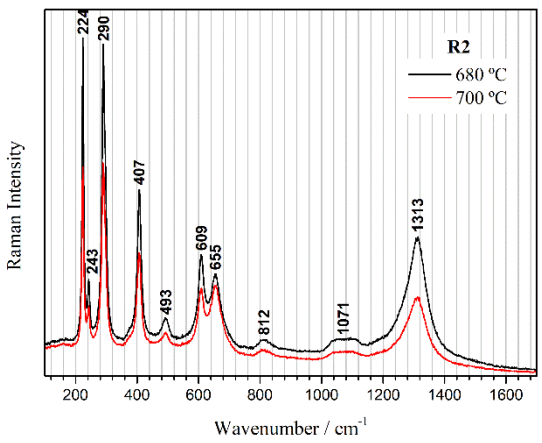


Figure 4.37 – Raman spectra of paint samples R2, fired at 680 ºC and 700 ºC.

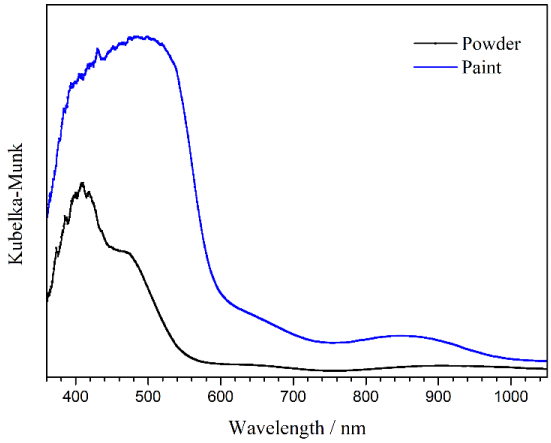
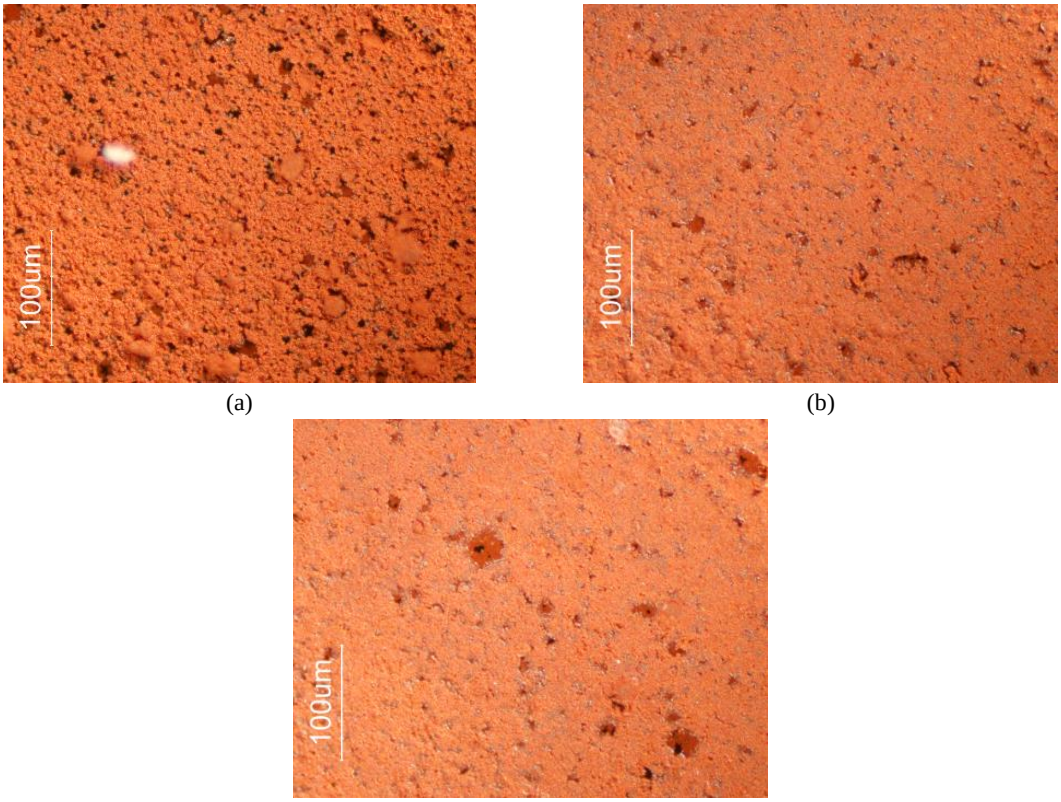


Figure 4.38– Absorption spectra of the sanguine recipe R2, both powder and paint samples.

Recipe R3

The paint samples for recipe 3 were prepared separately. This is a recipe that already presents gum arabic in the composition. Following the results above described, the use of gum arabic and water as a binder rendered better results, when the firing conditions were optimized. Can, in fact, the binding agent affect directly the outcome of the paint? Or it is just the heating rate that compromises the final result? Above *ca.* 300 ºC all the organic compounds are degraded, hence it is expected that

the binder will exclusively contribute to the application of the paint. However, it was verified in the previous section that the use of gum arabic as a binder proved to be more effective. On the other hand, by reducing the heating rate, and hence increasing the time needed to achieve the maximum firing temperature, more time is given for the paint to improve its adhesion to the base glass. In fact, by decreasing the heating rate, changes in the firing temperature, from 700 ºC to 680 ºC, might not be relevant. Henceforth, the paint samples were fired at 700 ºC, with three different heating rates: 5 ºC/min, 2 ºC/min, and 1 ºC/min. A fourth paint sample was fired at 680 ºC, with a heating rate of 2 ºC/min. A mixture of lavender oil and distilled turpentine was used as a binder.



(a) (b)

(c)

Figure 4.39 – Optical microscopy images of sanguine red paint recipe R3, fired at 700 ºC, with annealing rates of (a) 5 ºC, (b) 2 ºC, and (c) 1 ºC/ min.

Table 4.18 – Final results for sanguine powder and paint, at 680 ºC and 700 ºC, with a heating rate of 2 ºC / min.

Powder	**Paint**	
	680 ºC	700 ºC
		

Table 4.18 presents the results obtained (at 2 ºC/min as heating rate). The final result of both powder and paint closely resembled the traditional red carnation colour that is observed for historical stained-glass carnation paint. For the three heating rates good results were achieved in terms of the adhesion of the paint to the base glass, however, with heating rate of 5 ºC / min residues of the paint can still be removed from the surface, and with a heating rate of 1 ºC / min, the paint starts to penetrate the base glass. The best result was thus accomplished with a heating rate of 2 ºC / min (Figure 4.39).

The powder sample was characterized by infrared spectroscopy. Gum Arabic was identified through the characteristic stretching and bending absorption bands of hydroxyl, carboxyl and carbine groups. In addition, silicates were characterised through the Si-O and Si-O-Si vibrations (Derrick, Stulik and Landry, 1999) (Figure 4.40, and Table XII.3, Appendix XII).

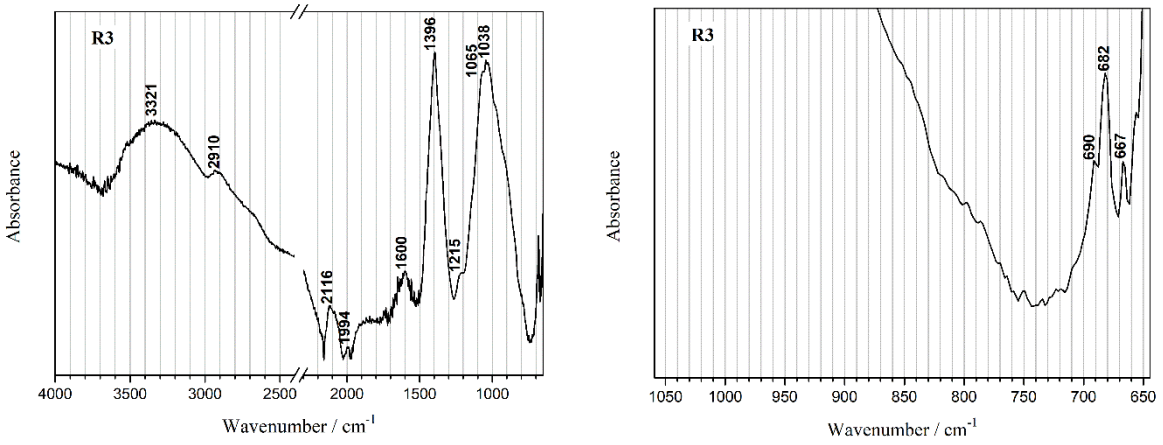


Figure 4.40 – Infrared spectrum of the powder sample R3. A detailed image of the absorption bands between 600 cm^{-1} and 700 cm^{-1} is presented in (b).

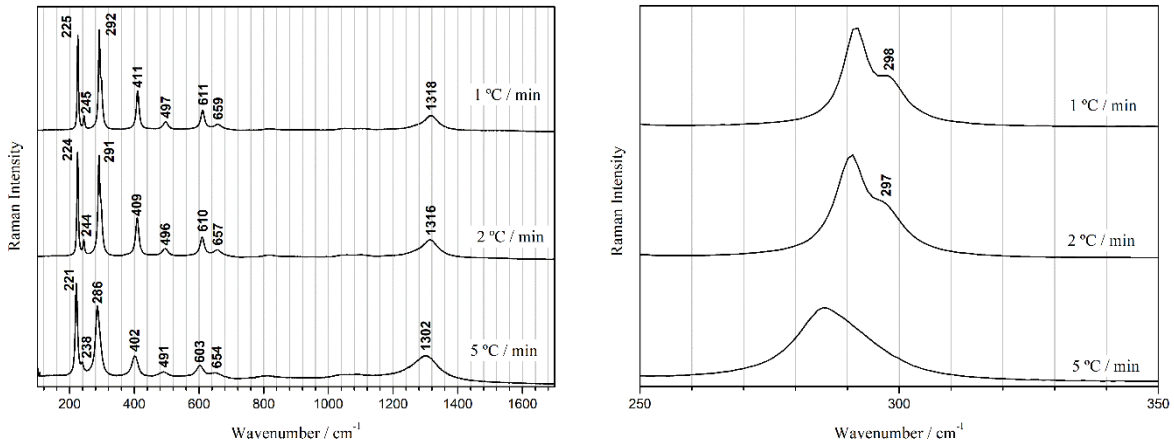


Figure 4.41 – Raman spectra of R3 paint samples fired at 700 ºC, with annealing rates of 5 ºC / min, 2 ºC / min and 1 ºC / min.

Unlike recipes R1 and R2, the iron compounds were not possible to identify through infrared spectroscopy and were identified by Raman spectroscopy of the paint samples. Hematite was identified through its characteristic Raman assignments (Legodi, 2008). The spectra of the paint fired with a heating rate of 5 ºC / min presents a deviation towards lower wavenumbers when compared with the samples fired at 2 ºC / min and 1 ºC / min. In addition, magnetite was identified with the presence of a band centred on 298 cm^{-1}, which appears with the decreasing of the heating rate (Figure 4.41, and Table XII.4, Appendix XII). Contrasting with recipe R2, no changes on the structure of the chromophore were visible between powder and paint sample (Appendix XIII).

Figure 4.42 – Heraldic panel *Iurgen von Brouck*. © Fernanda Barroso.

Concurrent to the reproduction of sanguine red recipes, it was possible to characterize sanguine red paint present on two stained-glass panels dated to between the 17th and 18th centuries, belonging to a 19th-century window assemblage from Ajuda National Palace. One of the panels is presented here, a heraldic panel dated probably to the 18th century. The panel is composed of a single colourless glass piece, painted with grisaille, yellow silver staining, blue enamel and sanguine red (Figure 4.42).

UV-Vis and Raman spectroscopy were performed to characterize the sanguine red paint (Figure 4.43). According to the results, the paint is in agreement with the results obtained for the reproduction of the paint recipe R3 (cf. Figure 4.41). The results identify hematite through its characteristic Raman assignment and absorbance spectrum.

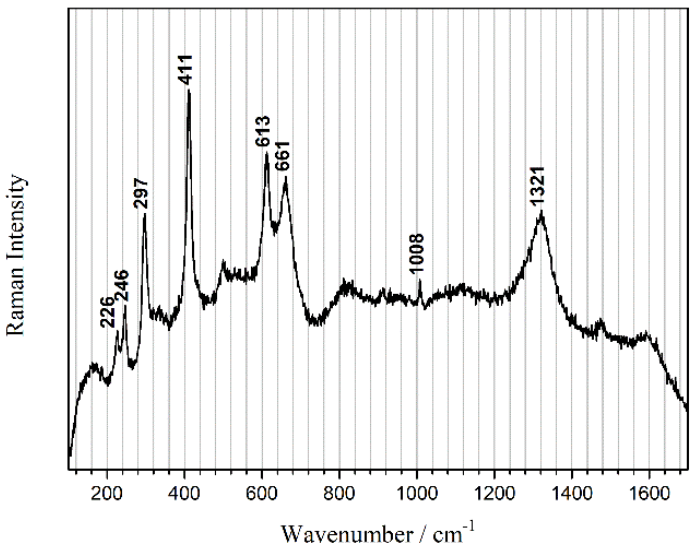


Figure 4.43 –Raman spectrum of the sanguine red paint of the Heraldic panel *Iurgen von Brouck*.

The reproductions obtained have revealed similar results to the example case study to which they were compared, evidencing a good agreement between the historical samples and the laboratory work. This study was later developed to an extended study of chemical and morphological characterization of both pigment and paint samples, with further studies of its adhesion to the glass substrate (Santos and Vilarigues, 2018).

4.3. Grisaille

4.3.1. The recipes

The grisaille painting was the first painted decoration to be used on stained glass. This paint was applied to depict on coloured and clear glass figures, motives and other details, as a thick opaque line, known as *grisaille à contourner*, or as a thin line, known as *grisaille à modeler* (Caen, 2009; Schalm *et al.*, 2009). One of the first references to the preparation of the grisaille paint is the one by Eraclius, *De coloribus et artibus romanorum*, dated to between the 10th and the 13th centuries:

> *VIII [271]. Take good and shining lead, and put it into a new jar, and burn it in the fire until it is reduced to powder. Then take it away from the fire to cool. Afterwards take sand and mix with that powder, but so that two parts may be of lead and the third of sand, and put it into an earthen vase. Then do as before directed for making glass, and put that earthen vase into the furnace, and keep stirring it until it is converted into glass. But if you wish to make it appear green, take brass filings, and put as much as you think proper into the lead glass; and then, it you wish to make any vase, do so with the iron tube. Afterwards take out this vase with the glass, and let it cool. You may, if you like, mix some of this leaden glass with a grossinum of sapphire for painting on glass, adding to it one-third part of scoria of iron. And this pigment is to be ground in an iron slab.*[30]

From the first historic recipes until the 19th century, grisaille recipes underwent minor changes. The first recipes prescribe the use of a glass with a high lead content, up to 60 % in weight. From the 17th century onwards recipes describe this lead glass as *rocaille*. From this point on the composition of the base glass stabilizes, reaching 75 % wt. of lead. Other components could be added. The medieval recipes of Eraclius and Theophilus prescribe the addition of *saffire* (alumina), and the Marciana manuscript, dated to the 16th century, the addition of ashes; Kunckel in his 17th-century treatise *Ars Vitraria Experimentalis* prescribes the addition of antimony and lead white. These components could also work as fluxes.

The source of iron and copper remained the same throughout time. The colourants were obtained persistently from the calcination of the respective metals, or from the recycling of metallic remains from smiths' workshops. This tendency changed in the 19th century when earths and ochres began to be used as a source of iron (Table 4.19).

The reproduction of the grisaille paints, and further chemical and morphologic characterization of both grisaille powder and paint was performed by Carla Machado, within the work of her Master project, entitled "Estudo de Producção de Grisalhas Históricas" (Study of the Production of Historic Grisailles) (Machado, 2016). The main results will thus be presented in the next sub-chapter.

[30] Merrifield, M., 1849. *Original treatises dating from the XIIth to XVIIth centuries, on the arts of painting, in oil, miniature, mosaic, and on glass; of gilding, dyeing, and the preparation of colours and artificial gems, volume I*, p. 216.

Table 4.19 – Historic recipes for the grisaille painting technique, date to between the 10th and the 17th centuries.

		Colourants					Fusion agents					Additives						Binders			
		Iron filings	Copper filings	Manganese	*Lápis Amótica* (Hematite)	Umber	Lead glass/ Jewish Glass/ Rocaille	Tin flux	Green glass	Yellow glass	Byzantine blue glass	German white glass	Calcined lead and/or tin	Ashes	Lime	*Grossinum* of Saphire	Antimony	Lead white	Gum arabic	Urine	Wine	Vinegar
Eraclius (10th-13th centuries)		X					X									X						
Theophilus *De diversibus artibus* (12th century)			X						X		X									X	X	
Antonio da Pisa *Memoria* (14th century)			X							X												
Marciana manuscript *Secreti diversi* (16th century)		X											X	X					X			
Giorgio Vasari *Le Vite* (16th century)		X	X		X														X			
Pierre Lebrun (17th century)		X					X								X					X		
Félibien *Des Principes* (17th century)		X					X												X			
Kunckel *Ars Vitraria Experimentalis* (1679)	1	X	X					X											X			
	2	X					X										X		X			
	3		X				X										X		X			
	4	X					X												X			
	5	X	X					X											X			
	6		X					X									X			X			
	7	X	X									X							X			
	8	X	X				X											X	X			
	9	X	X				X						X						X			
	10		X					X													X		
	11	X			X							X				X						X
	12				X			X													X		X
	13																						

4.3.2. The reproductions

Selected recipes were chosen for reproduction (highlighted in Table 4.19), according to the information provided. A multi-analytical approach was used to characterize chemic and morphologically both grisaille powder and paint samples, before and after the firing process (Machado, 2016). The production of the paint recipes was divided into four steps:

1) The production of the selected lead base glass;
2) The preparation of the metallic oxides;
3) The mix and homogenization of all the components;
4) The application of the grisaille paint with gum arabic, firing the samples at 680 ºC for 30 minutes, with a heating rate of 3 ºC/min.

Table 4.20 – Recipes for lead glass used for the productions of the grisailles.

Recipes	Glass production	Composition (wt. %)
Eraclius (10th century) / Antonio da Pisa (14th-15th century)	*De coloribus et artibus Romanorum*, Eraclius	Two components $PbO:SiO_2$ 2:1 (w/w)
Theophilus (12th century)	*De coloribus et artibus Romanorum*, Eraclius	Three components $PbO:SiO_2:CuO$ 8:4:1 (w/w/w)
Kunckel (17th century)	*L'Art de la peinture sur verre et de vitrerie,* Pierre Le Viel	Two components $PbO:SiO_2$ 3:1 (w/w)

Table 4.21 – Proportion between the colourants and the base glass used for each grisaille.

Recipes		Colourant:Base glass (w:w)
Eraclius (10th century)		1:1
Theophilus (12th century)		1:2
Pisa (14th-15th century)		1:2
Kunckel (17th century)	2	1:1
	3	1:1
	8	3:3
	9	1.5:1

One of the main components of a grisaille is the lead glass, also called *rocaille*, which acts as a flux, and contributes to a proper adhesion of the paint to the glass substrate. Several recipes for lead glass were produced, according with the information provided by the treatises. For the productions of the grisailles according to Eraclius and Kunckel, the recipes for the lead glass were also found on those treatises. In the case of the grisaille recipes provided by Theophilus and Antonio da Pisa, it was necessary to use

recipes from other treatises from a coeval period (Table 4.20). The proportion between the colourants used for each recipe (iron and/or copper) and the base glass are presented in Table 4.21.

The final results for pigment and painted grisailles, before and after firing, is presented in Figure 4.44. For the majority of the samples, a change on the colour is visible after the firing process, mainly the ones with copper as the main colourant. The adhesion of the paint to the base glass is variable, and in some cases the paint presents a more glassy appearance, such as the one obtained by the recipe of Antonio da Pisa, when compared with others which resulted in a dull appearance, with a roughened surface, such is the case of the grisaille obtained by Theophilus' recipe.

Figure 4.44 – The results obtained for the grisaille paint reproductions, both powder and paint samples.

The grisaille paint samples from Eraclius and Theophilus present a heterogeneous surface with the presence of several inclusions rich in aluminium, unlike the one from Antonio da Pisa, which does not present any inclusions. The good adhesion of the grisailles to the base glass is confirmed by the diffuse interface between the paint layer and the base glass. EDS maps do also confirm the dispersion of the metallic oxides on a lead-rich matrix (Figure 4.45)

In relation to the grisaille paint samples produced according to Kunckels' recipes, we can see that the paint layer, even though with a heterogeneous surface, present fewer inclusions when compared with the grisailles obtained after the medieval recipes. To what concerns the interface between the paint layer and the base glass, only the grisaille paint recipe 8 presents a similar interface compared with the previous ones, which might be related with the addition of a second source of lead (lead white) as a flux (Figure 4.46). Grisaille paint recipe 9 clearly shows that the firing temperature, or firing time, was not sufficient since we can see many inclusions, not only of the metallic oxides but also rich in lead, contrarily to the typical lead-rich matrix. In addition, the EDS map shows a lead-rich area at the upper area of the base glass (Figure 4.47).

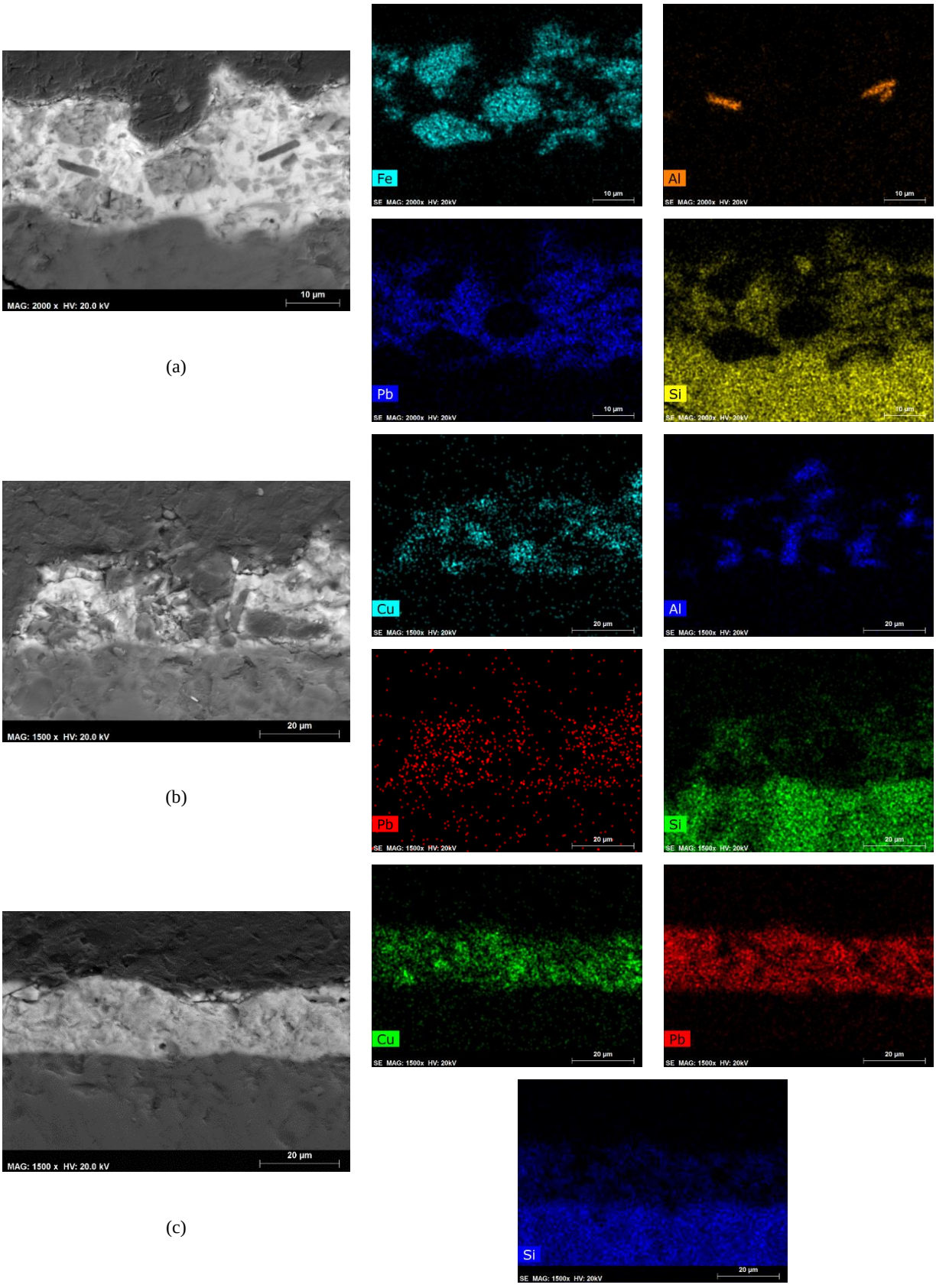


Figure 4.45 – SEM-BSE image with EDS maps of the cross-section of the grisaille paint reproduced according to (a) the recipe by Eraclius, (b) the recipe by Theophilus, and (c) the recipe by Antonio da Pisa.

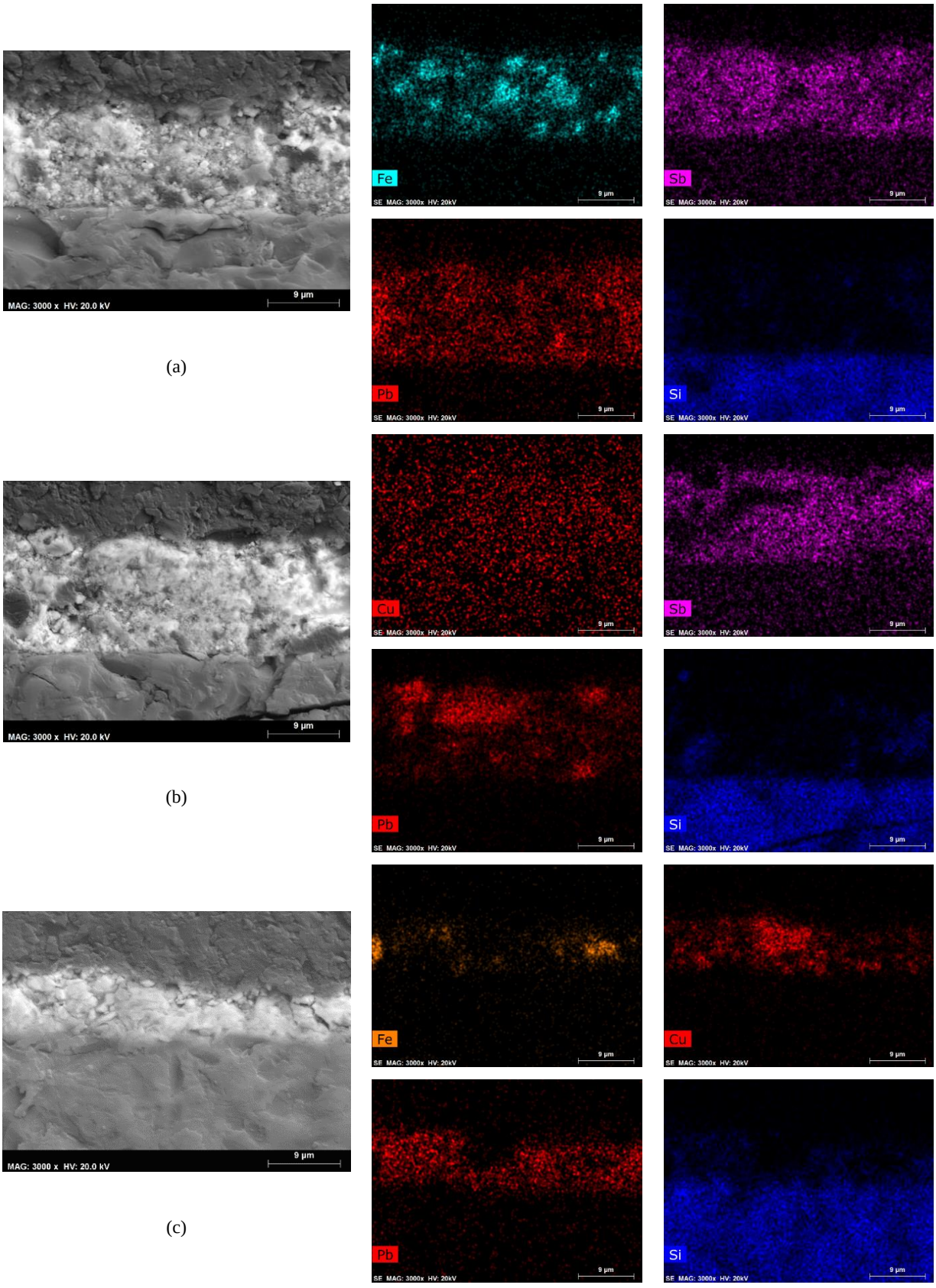


Figure 4.46 - SEM-BSE images with EDS maps of the cross-section of the grisaille paint reproduced according to the recipes by Kunckel: (a) recipe 2, (b) recipe 3, and (c) recipe 8.

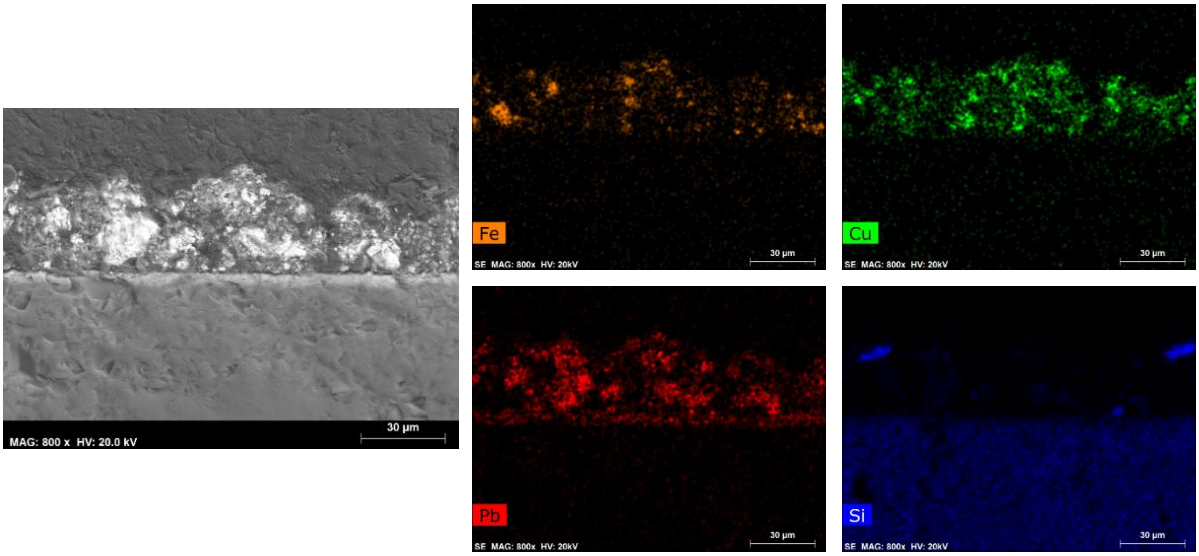


Figure 4.47 – SEM-BSE images with EDS maps of the cross-section of the grisaille paint recipe 9, reproduced according to the recipes by Kunckel (17th-century).

µ-PIXE and XRD analysis were performed on powder samples, before and after the firing process (Machado, 2016). The results obtained (Table 4.22) reveal a decrease of the lead content, related with the diffusion of this component to the base glass. Regarding the addition of antimony oxide, we can also see that its content decreases after firing. The role of antimony in the production of grisaille painting is not well defined: in glass production it was used as an opacifier and as a fining agent on low melting temperature glass (Navarro, 2003).

Concerning the crystallographic phases identified prior the firing process, hematite (Fe_2O_3) and magnetite (Fe_3O_4), cuprite (Cu_2O) and tenorite (CuO) were identified for the iron- and copper-rich grisailles, respectively. Other crystallographic phases were also identified related with aluminium and antimony, such as corundum (Al_2O_3) and senarmontite (Sb_2O_3). After the firing process, magnetite is converted into hematite as a result of the oxidation of the metals, associated with a change in the final colour, from black to brownish coloured grisailles. The same result occurred for the copper-rich grisailles, with a transformation of cuprite to tenorite, leading to a colour change from brown to black (Eastaugh *et al.*, 2004). Regarding the addition of antimony oxide, we can verify the transformation of senarmontite to cervantite (Sb_2O_4), and the formation of crystallographic phases with copper and lead, such as copper and antimony oxide $CuSb_2O_6$, bindheimite ($Pb_2Sb_2O_7$), and rosiaite ($PbSb_2O_6$) (Machado, 2016).

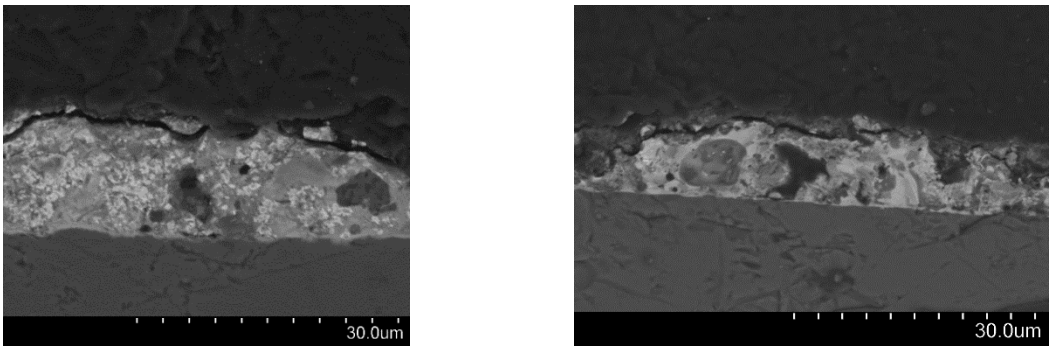
Table 4.22 - Chemical and crystallographic composition of the produced grisailles before (B) and after (A) the firing process.

			Final composition (wt.%)							Crystallographic phases	
			Al_2O_3	SiO_2	Fe_2O_3	CuO	PbO	Sb_2O_5	Other		
Eraclius		*B*	4.44	25.95	32.28	-	36.71	-	0.62	Fe_2O_3 Fe_3O_4	Hematite Magnetite
		A	4.15	23.82	40.19	-	30.85	-	0.98	Fe_2O_3	Hematite
Theophilus		*B*	42.26	8.19	-	31.38	18.13	-	0,05	Cu_2O Al_2O_3	Cuprite Corundum
		A	42,67	9,08	-	30,96	16,91	-	0,38	CuO Al_2O_3	Tenorite Corundum
Pisa		*B*	-	19,91	-	35,03	45,07	-	-	Cu_2O CuO	Cuprite Tenorite
		A	-	24,61	-	33,32	41,60	-	0,47	CuO	Tenorite
Kunckel	R2	*B*	-	8,35	37,68	-	33,11	20,18	0,59	Fe_2O_3 Fe_3O_4 Sb_2O_3	Hematite Magnetite Senarmontite
		A	-	11.20	41.42	-	31.61	14.90	0.77	Fe_2O_3 $Pb_2Sb_2O_7$ Sb_2O_4	Hematite Bindheimite Cervantite
	R3	*B*	-	9.86	-	42.24	27.13	20.56	0.18	Cu_2O Sb_2O_3	Cuprite Senarmontite
		A	-	10.57	-	42.29	30.66	16.45	-	CuO $CuSb_2O_6$ $PbSb_2O_6$	Tenorite Tri-rutile Rosiaite
	R8	*B*	-	9.01	13.96	34.21	42.71	-	0.09	CuO Cu_2O Fe_2O_3 Fe_3O_4 PbO	Tenorite Cuprite Hematite Magnetite Litharge
		A	-	9.53	14.47	35.66	40.11	-	0.22	CuO Fe_2O_3 Fe_3O_4 $Pb_8Fe(Si_2O_7)_3$	Tenorite Hematite Magnetite -
	R9	*B*	-	6.55	14.55	35.55	43.03	-	0.05	CuO Cu_2O Fe_2O_3 Fe_3O_4 PbO	Tenorite Cuprite Hematite Magnetite Litharge
		A	-	7.57	16.39	34.82	40.94	-	0.27	CuO Fe_2O_3 Fe_3O_4 $Pb_8Fe(Si_2O_7)_3$	Tenorite Hematite Magnetite -

The reproduced grisaille paints were compared with historic grisailles from Batalha Monastery, Tomar and Pena National Palace. The study of two 16th-century historic grisailles paints from Batalha Monastery (sample J18) and Convento de Cristo in Tomar (sample T01) was performed by Sara Louro in the frame of the Master project, entitled "O Vitral e as suas tintas: Grisalha e Amarelo de Prata" (Stained Glass and its paints: Grisaille and Yellow Silver Staining).

The results obtained by µ-PIXE reveal a lead-rich silicate matrix with iron as the main pigment. Sample J18 contains 11.7 wt.% Fe_2O_3, and 31.7 wt.% PbO. The amount of CuO is negligible. Sample T01 contains 31.24 wt.% Fe_2O_3, 5.22 wt.% CuO, and 22.7 wt.% PbO. The amount of flux relative to the pigment ($PbO/(Fe_2O_3+CuO+PbO)$) is 73 wt.% for sample J18, and 38 wt.% for sample T01 (Louro, 2017). The results for sample T01 are in agreement with the results in the literature for 16th-century grisaille paint samples. As for the grisaille paint sample J18 the amount of flux relative to the pigment is higher when compared with the results of the literature (Pradell *et al.*, 2016).

SEM/EDS analyses to both samples revealed a heterogeneous paint layer (Figure 4.48). The interface paint layer/ base glass for the grisaille paint sample J18 from Batalha Monastery is smoother when compared to the interface of sample T01 from Tomar, revealing a good diffusion of lead, improving the adherence between the grisaille paint layer and the base glass.



(a) (b)

Figure 4.48 – SEM/BSE images of the 16th-century grisaille paint samples from (a) Batalha Monastery, and (b) Convento de Cristo in Tomar.

Stained glass fragments dated to between the 16th and 17th centuries, from Pena National Palace and Vitrocentre Romont, were also chemical and morphologic characterized[31].

The description of the given fragments is reported in the sub-chapter 4.1.3 (pp. 64-66).

The results of µ-PIXE analyses (Table V.2, Appendix V) on grisaille paints from samples of both sets show that it is composed of a lead-rich silicate matrix containing iron and copper components as pigments. One of the samples of the VCR set (VCR05) contains 17.5 wt.% Fe_2O_3, 4.7 wt.% CuO and

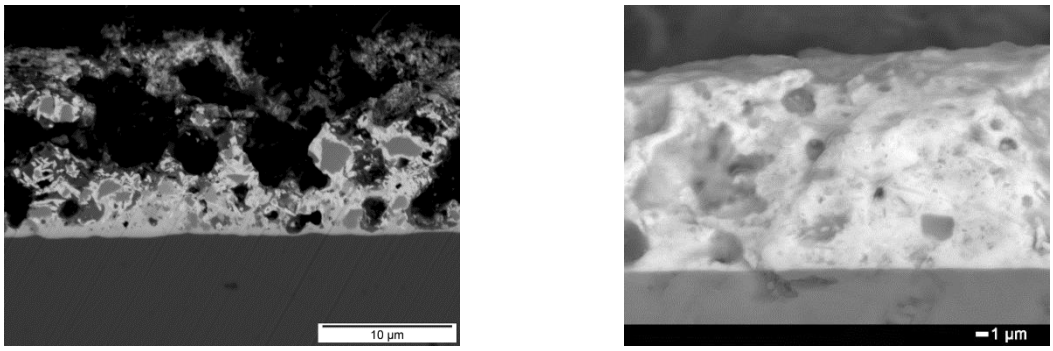
[31] The results of this section are published in: Machado, A. *et al.* (2017) 'Swiss Kabinettscheiben from a 19th century Portuguese collection. Study and chemical characterisation', in Wolf, S. and Pury-Gysel, A. de (eds) *Annales du 20e Congrès de l'Association International pour l'Histoire du Verre, Fribourg/Romont, 7-11 Septembre 2015*. Romont: AIHV - Association Internationale pour l'Histoire du Verre, pp. 684–688; Machado, A. *et al.* (2017) 'Swiss Stained-Glass Panels: An Analytical Study', *Microscopy and Microanalysis*, 23(4), pp. 878–890. DOI: 10.1017/S1431927617000629.

31.7 wt.% PbO. Similar results are found for grisaille paints from the 16th century (Vilarigues and Da Silva, 2004; Carmona, Villegas and Navarro, 2006; Pradell *et al.*, 2016). Sample VCR12 has inverted iron and copper concentrations (6.4 wt.% Fe_2O_3,18.5 wt.% CuO); the lead concentration is similar to that of VCR05 (42.8 wt.% PbO). The amount of flux relative to the pigment ($PbO/(Fe_2O_3+CuO+PbO)$) is 59 wt.% for sample VCR05 and 63 wt.% for sample VCR12; these results are in agreement with the ones obtained for grisaille paints dating to the 17th century (Pradell *et al.*, 2016). When analysed, the grisaille on samples from the PNP set show slightly lower flux to pigment ratios: the grisaille on PNP05 has a ratio of 43 wt.% and PNP17 has a ratio of 57 wt.%. This latter sample also contains 2.6 wt.% Ag_2O, which is due to the fact that this sample is also painted with silver stain on the backside of the stained glass fragment.

SEM/EDS analysis of the grisaille layers revealed varying thicknesses for the grisaille layers: in sample VCR05 its thickness ranges between 20 µm and 50 µm, in sample PNP06 it varies between 2 µm and 10 µm (Figure 4.49). The grisaille layer in sample VCR05 is more porous and heterogeneous than that of PNP06, but both samples contain iron grains of various sizes surrounded by a lead-rich matrix (cf. Figure 4.48a).

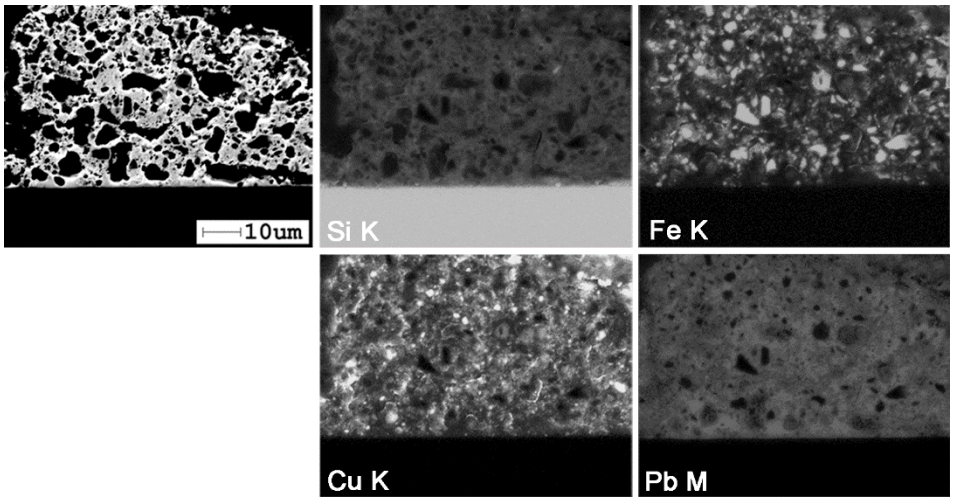
The interface between the grisaille and the base glass is smooth in both samples, suggesting that the lead diffused into the glass well and that there is a good adherence between the paint layer and the glass. This is evidence of the high quality of the grisaille painting, which was properly burnt in during the firing process.

SEM/EDS maps of the grisaille layers in samples VCR05 and PNP06 reveal the even distribution of the iron and copper pigment particles. The lead is finely dispersed in the matrix (Figure 4.50). The production process of the grisaille explains this morphology. The grisaille paint layers are fixed to the glass at firing temperatures of around 600 to 750 ºC. At these temperatures, the lead compound melts completely, whereas copper and iron pigments, which have higher melting temperatures, remain solid (Vilarigues and Da Silva, 2004).

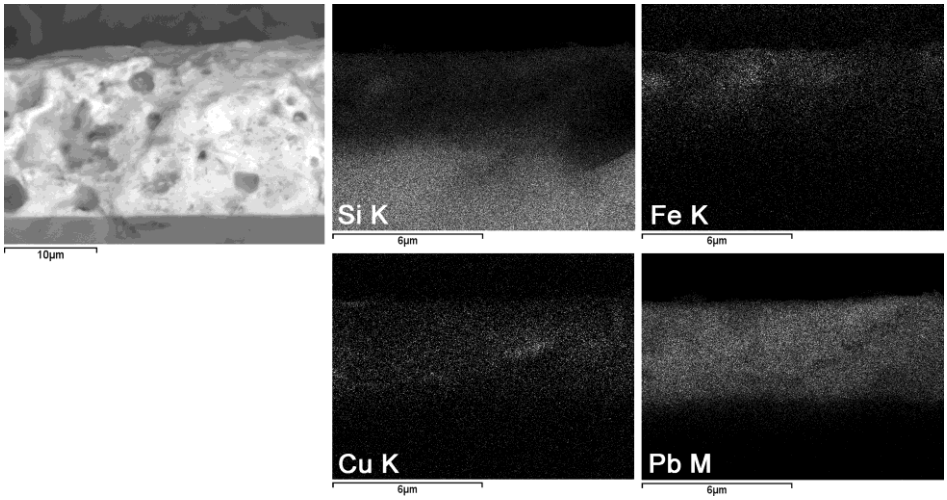


(a) (b)

Figure 4.49 – SEM/BSE images of grisaille layer in sample (a) VCR05 and (b) sample PNP06.



(a)



(b)

Figure 4.50 – SEM/EDS maps for the grisaille layers of (a) sample VCR05, and (b) sample PNP06.

The results obtained for the case studies were in good agreement with the ones obtained for the reproduced grisailles. The grisaille paint from Batalha Monastery and Convento de Cristo in Tomar presented similar results to the one obtained from 12th century Theophilus manuscript. The grisaille paint from the case studies of Pena National Palace and Vitrocentre Romont are comparable with the reproductions of the grisaille paint according to Kunckel's 17th-century treatise, presenting a more homogeneous layer when compared with the ones from Batalha and Tomar. They also present iron and copper inclusions, however of smaller size, like the grisailles from Kunckel's recipes. It is possible to verify that Medieval grisaille recipes were widely used until the 17th century when a new variety of recipes appeared, with the addition of other components to the recipes (Holbach, 1752).

The combination of laboratory work with the study of selected case studies proved that the choice of this methodology was successful.

CONCLUSIONS AND FUTURE WORK

The present study was focused on the study of historic painting techniques applied to stained glass, namely blue enamels, sanguine red, and grisaille, with special emphasis on blue enamel painting.
This study started with the research and interpretation of recipes from a selected group of historical treatises, dated to between the 10th and the 18th centuries. During the Medieval period knowledge was confined to workshops, either in a religious or urban context (although knowledge circulate between the workshops). *De diversibus artibus*, the 12th-century treatise written by Theophilus, is the example of what we believe to be a recollection of the activity carried in his monastery. Presumably, the intention could be to gather all the important information into one book, to be given to the overseer of the workshop. In other manuscripts, we can see the compilation of specific recipes copied from other manuscripts, which were certainly of more interest to the workshop. The Lucca Manuscript, *Mappae Clavicula*, and *Eraclius* are good examples. Many stained-glass artists and practitioners imparted their thoughts and expertise, such as Antonio da Pisa or the monk of Zagan, whose treatises are specific for glass painting, and written for artisans already familiar with stained glass making.
What began as described by Paul Engle (2014) as "books of secrets", was later published and transmitted to the public. The 17th-century treatise *L'Arte Vetraria* by Antonio Neri changed this framework, embodying the know-how exclusive from the workshops into a systematic publication of glass and glassmaking, with an extensive description of the selection and treatment of the raw materials to be used. Antonio Neri revealed the secrets behind the production of a glass of high quality, showing the different considerations that one must give to the choice of the materials, the ones that could be imported and the ones that could be collected locally. Even so, it was a work directed to glassmaker.
The work of Antonio Neri was indeed of major importance to set a pattern for the Early-modern and Modern periods. His work can be revisited on Merret's *The Art of Glass* (1662), Kunckel's *Ars Vitraria Experimentalis* (1679), and Pierre Le Vieil's *L'Art de la Peinture sur Verre et de la Vitrerie* (1774).

The characterization of selected raw materials, used for the production of blue enamels, was performed according to the instructions provided by the works of Antonio Neri and Kunckel. The reproduction of selected recipes of blue enamels and sanguine red was performed (according to selected recipes from 17th-century treatises), followed by a multi-analytical approach to chemical and morphologically

characterize both powder and paint samples. This methodology was also performed for the reproduction of grisaille paint, in the frame of a master project.
A good correlation between the information provided by the treatises and the laboratory work was established, placing in evidence the importance of the intersection between the written sources and the practical work, which has been highly valued in these past years.

The results obtained for blue enamels show that the use of zaffer as a colouring agent does not allow determination of the outcome of the paint while adding powdered glass such as smalt gives glass painter the opportunity to know the final result before firing. The comparison of reproduced paints with a set of stained-glass panels from Pena National Palace, allowed to propose that smalt was the colouring agent used to produce the historical enamels. Corrosion studies were performed on both powder and enamel paint samples, aiming at understanding its corrosion mechanisms. The increase of the pH of the electrolyte reveals an ionic exchange between the alkaline ions (namely K^+) of the glass and the hydrogen-bearing ions of the water. With the lixiviation of the alkaline components, cobalt will be influenced by other neighboring ions, leading to the change of colour. Furthermore, the infrared analysis reveals the presence of lead carbonate in the pristine samples, which can indicate that this compound is formed during the heating process.
Regarding the paint samples, their exposure to high relative humidity resulted in the deposition of moist at the surface of the paint layer, attested by an increase of the L* coordinate. In addition, Na-rich micro-crystals were formed.
Concerning the reproductions of the sanguine red paint, it was concluded that the sanguine recipe R3, from the 18th-century historic treatise *L'Art de la Peinture sur Verre et de Vitrerie*, by Pierre Le Vieil, showed good results, in agreement with the sanguine red paint perceived in historically stained glass fragments. Testing several parameters, such as the binder used, firing temperature and annealing rate, the sanguine paints painted with a mixture of gum arabic and water, and fired at 700 ºC with an annealing rate of 2 ºC / min, presented better results on the adhesion between the paint layer and the base glass.
As for grisaille reproductions, looking to the historical sources, we see that the main components of the grisaille - colorant and fusing agent – remained the same over time, except in the 19th century, where the typical metal oxides of copper and iron, were replaced by the use of earth pigments, such as hematite and umber.
The main differences found in the recipes lay on the composition of the lead-based glass and on the ratios between this and the coloring agents.
Furthermore, it was also possible to conclude that there is an evolution of the morphology of the grisailles towards a higher homogeneity of the surface throughout the centuries. Cross-section analyses through SEM-EDS analysis with BSE imaging allowed to verify that the grisailles from the 17th century present fewer inclusions when compared with the ones from the Medieval period, which can have an impact on its mechanical behavior.

The reproductions were compared with selected case studies from Pena National Palace, Convento de Cristo in Tomar, and Batalha Monastery. In the case of the samples from Pena National Palace and Vitrocentre Romont, different recipes seem to have been used to make the blue enamels. However, the cobalt ore used as a coloring agent in all of the blue enamels is likely to have come from the same mining district in Schneeberg, Germany. The morphological characteristics identified in some of these samples are in agreement with the results obtained for the two skutterudite samples analysed in this study. Concerning the grisaille paint, samples from the three collections were compared with the reproductions performed in the frame of the master project by Carla Machado. A good agreement was established between the grisaille paint reproductions and the case studies. The grisaille paint from the stained-glass samples from Batalha and Tomar present a lead-rich silicate matrix, with iron as the main pigment, whereas the grisaille paint from the stained-glass samples from Pena National Palace and Vitrocentre Romont present iron and copper as pigments, also dispersed in a lead-rich silicate matrix. The morphological characteristics of the paint layers studied are comparable with the reproductions of the grisaille paint according to Kunckel's 17th-century treatise.

This combination of written sources with hands-on experience can raise many questions. Looking to the recipes of Neri's treatise, we see the addition of a lead and tin calx to the base glass used for enamel production. A research on the archaeometric studies on enamel painting in stained glass allows us to assess that tin oxide is many times not present in the blue enamel painting compositions that we find, despite many recipes for blue enamel painting from the 17th century onwards, being translations of Neri's work, do prescribe the addition of tin. Regardless of the many translations and the continuity of the recipes throughout the centuries, it seems that some information remains hidden. We know that the addition of tin can opacify the paint layer, therefore we can assume that this detail was acknowledged and therefore it was not necessary to change or to advise the removal of this component from the recipe: glassmakers already knew that tin was not necessary. It should be underlined the difference between how it must be done, according to the written information, and how it is done, according to the practical knowledge.

Future work

This thesis is focused on the characterization of enamel painting, sanguine red, and grisaille, with special emphasis on blue enamels. The present work was successful in providing new insights on the colour characterization of these paints, and on the corrosion mechanisms associated with blue enamel painting. Related to enamel paint, it is important to continue the research, reproduction, and characterization of this glass-based paint for other colours, implementing the same methodology, with a chemic and morphologic characterization of both powder and paint samples, with further degradation studies.

The study of the thermal behaviour of the enamel paint and the adhesion between the enamel layer and base glass is planned, through thermal compatibility tests using dilatometry and differential scanning calorimetry (DSC).

Related to the sanguine red paint, the results obtained have revealed that, in fact, to choose the best method of application of the paint is the best way to prevent further degradation. Yet, corrosion studies to both powder and paint samples are important to access possible colour changes and loss of adhesion to the base glass. Further analyses to the function of the binder in the adhesion of the paint to the base glass are also necessary. Finally, the research must carry on to the historic recipes which present copper as a colourant in addition to iron.

In addition to continue the research on glass paints, it is important to perform further archeometric and morphological studies of historical stained-glass paints, to assess the overall composition of these paints, the similarities and differences that we may find in terms of the recipes used, raw materials and their provenance.

REFERENCES

Agricola (1950) *De Re metallica*. Edited by H. Hoover and L. H. Hoover. Translated by H. C. Hoover and L. J. Hoover. New York: Dover Publications, Inc.

Ahmed, A. A. and Youssof, I. M. (1997) 'Reactions between water and lead crystal glass (24% PbO)', *Glass Technology*, 38(1), pp. 30–38.

Attard-Montalto, N. and Shortland, A. (2014) '17th century blue enamel on window glass from the cathedral of Christ Church, Oxford', *Journal of Cultural Heritage*, 16(3), pp. 365–371. doi: 10.1016/j.culher.2014.06.011.

Bacci, M. *et al.* (2007) 'The ancient stained windows by Nicolò di Pietro Gerini in Florence. A novel diagnostic tool for non-invasive in situ diagnosis', *Journal of Cultural Heritage*, 8, pp. 235–241. doi: 10.1016/j.culher.2007.02.001.

Bacci, M. and Picollo, M. (1996) 'Non-destructive spectroscopic detection of cobalt(II) in paintings and glass', *Studies in Conservation*, 41(3), pp. 136–144. doi: 10.1179/sic.1996.41.3.136.

Ball, P. (2007) *The Devil's Doctor*. London: Arrow Books.

Baroni, S., Brun, G. and Travaglio, P. (2013) 'Creation and Colouration of Stained-Glass Windows in Medieval Literary Sources: New Perspectives on Technical Treatises Dated Between the 12th and 16th centuries', in Römich, H. and Campagne, K. van L. (eds) *Recent Advances in Glass, Stained Glass and Ceramics Conservation, ICOM-CC Working Group Glass and Ceramics Interim Meeting and Forum of the International Scientific Committee for the Conservation of Stained Glass (Corpus Vitrearum-ICOMOS)*. The Netherlands: Spa Uitgevers, pp. 133–140.

Barros, C. V. da S. (1983) *O Vitral em Portugal, Séculos XV-XVI*. Lisboa: Comissariado para a XVII Exposição Europeia de Arte, Ciência e Cultura,.

Beckmann, J. (1846) *A history of inventions, discoveries, and origins*. Translated by W. Johnston. London: Richard and John E. Taylor.

Beretta, M. (2007) *The Alchemy of Glass: Counterfeit, Imitation, and Transmutation in Ancient Glassmaking*. USA: Science History Publications.

Beretta, M. (2014) 'Material and Temporal Powers at the Casino di San Marco (1574–1621)', in Dupré, S. (ed.) *Laboratories of Art, Alchemy and Art Technology from Antiquity to the 18th Century*. Cham: Springer International Publishing, pp. 129–156. doi: 10.1007/978-3-319-05065-2.

Bergmann, U. *et al.* (2006) *Stained Glass, an introduction based on examples from the Vitromusée Romont and the surronding region*. Villars-sur-Glâne: Imprimerie MTL SA.

Bischoff, G. (2002) *Das De Mayerne-Manuskript: die Rezepte der Werkstoffe, Maltechniken and Gemälderestaurierung*. Staatliche Akademie der Bildenden Künste.

Boer, P. and Engle, P. (2010) 'Antonio Neri: an annotated bibliography of primary references', *Journal of glass studies*, pp. 51–67.

Boesch, P. (1955) *Die Schweizer Glasmalerei*. Basel: Birkhäuser Verlag Basel.

Bontemps, G. (1868) *Guide du Verrier*. Paris: Librairie du Dictionnaire des Arts et Manufactures.

Boon, J. J. *et al.* (2001) 'Imaging Microspectroscopic, Secondary Ion Mass Spectrometric and Electron Microscopic Studies on Discoloured and Partially Discoloured Smalt in Cross- sections of 16th Century Paintings', *Chimia International Journal for Chemistry*, 55(11), pp. 952–960.

Boulanger, K. (2004) 'Les traités médiévaux de peinture sur verre', *Bibliothèque de l'école des Chartes*, 162(1), pp. 9–33. doi: 10.3406/bec.2004.463329.

Brady, G. and Clauser, H. (1989) *Materials Handbook*. New York: McGraw-Hill.

Brems, D. *et al.* (2012) 'Western Mediterranean sand deposits as a raw material for Roman glass production', *Journal of Archaeological Science*. Elsevier Ltd, 39(9), pp. 2897–2907. doi: 10.1016/j.jas.2012.03.009.

Brisac, C. (1989) *A thousand years of stained glass*. England: Macdonald&Co (Publishers) Ltd.

Brown, S. and O'Connor, D. (1991) *Glass-painters*. London: British Museum Press.

Bugslag, J. (2008) 'The Revival and Resurgence of Stained Glass "Treatises" in the 19th Century and their Implications for the Study of Pre-Modern Stained Glass', in Boulanger, K. and Hérold, M. (eds) *Le Vitrail et les traités du Moyen Âges à nous jours, Actes du XXIIIe colloque international du Corpus Vitrearum, Tours, 3-7 juillet 2006*. Bern: Peter Lang, pp. 297–314.

Burgio, L., Clark, R. J. and Firth, S. (2001) 'Raman spectroscopy as a means for the identification of plattnerite (PbO2), of lead pigments and of their degradation products.', *The Analyst*, 126(2), pp. 222–227. doi: 10.1039/b008302j.

Caen, J. (2009) *The production of stained glass in the county of Flanders and the duchy of Brabant from the XVth to the XVIIIth centuries: materials and techniques*. Antwerp: Brepols.

Cannon, L. (1991) *Stained glass in the Burrel collection*. Edinburgh: W & R Chambers Ltd.

Carmona, N., Villegas, M. A. and Navarro, J. M. F. (2006) 'Study of glasses with grisailles from historic stained glass windows of the cathedral of León (Spain)', *Applied Surface Science*, 252(16), pp. 5936–5945. doi: 10.1016/j.apsusc.2005.08.023.

Ceglia, A. *et al.* (2012) 'Cobalt absorption bands for the differentiation of historical Na and Ca/K rich glass', *Surface and Interface Analysis*, 44(2), pp. 219–226. doi: 10.1002/sia.3810.

Cianchetta, I. *et al.* (2012) 'Discoloration of the smalt pigment: experimental studies and ab initio calculations', *Journal of Analytical Atomic Spectrometry*, 27(11), p. 1941. doi: 10.1039/c2ja30132f.

Cílová, Z. and Woitsch, J. (2012) 'Potash – a key raw material of glass batch for Bohemian glasses from 14th–17th centuries?', *Journal of Archaeological Science*, 39(2), pp. 371–380. doi: 10.1016/j.jas.2011.09.023.

Colomban, P., Milande, V. and Le Bihan, L. (2004) 'On-site Raman analysis of Iznik pottery glazes and pigments', *Journal of Raman Spectroscopy*, 35(7), pp. 527–535. doi: 10.1002/jrs.1163.

Cornell, R. M. and Schwertmann, U. (2003) *The Iron Oxides. Structure, Properties, Reactions, Occurrences and Uses*. 2nd edn. Weinheim: WILEY-VCH Verlag GmbH & Co.

Coutinho, I. *et al.* (2016) 'Fensterbierscheiben in the Pena National Palace collection - chemical and iconographic relations', *X-Ray Spectrometry*, 45(6), pp. 308–317. doi: 10.1002/xrs.2706.

Debitus, H. (1991) 'Recherche pour une formulation nouvelle de grisailles', *Science et Technologie de la Conservation et de la Restauration des oeuvres d'art et du patrimoine*, (2), pp. 24–29.

Delgado, J. (2010) *Vitrais da Charola do Convento de Cristo em Tomar – história e caracterização*.

Universidade NOVA de Lisboa.

Delgado, J. *et al.* (2011) 'Characterisation of medieval yellow silver stained glass from Convento de Cristo in Tomar, Portugal', *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*. Elsevier B.V., 269(20), pp. 2383–2388. doi: 10.1016/j.nimb.2011.02.059.

Delgado, J. M. *et al.* (2015) 'Characterization of a Novel Intrinsic Luminescent Room-Temperature Ionic Liquid Based on [P6,6,6,14][ANS]', *Chemistry - A European Journal*, 21(2), pp. 726–732. doi: 10.1002/chem.201402534.

Delgado, J. M. *et al.* (2017) 'The effect of three luminescent ionic liquids on corroded glass surfaces – A first step into stained-glass cleaning', *Corrosion Science*, 118, pp. 109–117. doi: 10.1016/j.corsci.2017.01.027.

Derrick, M. R., Stulik, D. and Landry, J. M. (1999) *Infrared Spectroscopy in Conservation Science*. Los Angeles: The Getty Conservation Instiute.

Dias, P. (1994) *A Arquitectura Gótica Portuguesa*. Lisboa: Editorial Estampa.

Dossie, R. (1758) *The Handmaid to the Arts*. London: J. Nourse.

Downs, B. *et al.* (2017) *RRUFF Project*. Available at: http://rruff.info.

Dungworth, D. and Brain, C. (2005) *Investigation of Late 17th Century Crystal Glass*, *Centre for Archaeology*.

Eastaugh, N. *et al.* (2004) *Pigment Compendium*. Oxford: Butterworth-Heinemann.

Engle, P. (2003) *L'Arte Vetraria / The Art of Glass*. Translated by P. Engle. Massachusetts: Heiden & Engle.

Engle, P. (2014) *Conciatore: The Life and Times of 17th Century Glassmaker Antonio Neri*. Massachusetts: Heiden & Engle.

Félibien, A. (1697) *Des principes de l'architecture, de la sculpture, de la peinture, et des autres arts qui en dépendent : avec un Dictionnaire des termes propres à chacun de ces arts*. 3rd edn. Paris: Veuve & Jean Baptiste Coignard, fils.

Freestone, I. (1992) 'Theophilus and the composition of Medieval Glass', *Materials Research Society*, 267(739), pp. 739–745. doi: https://doi.org/10.1557/PROC-267-739.

Friedrich, K. and Mayhoff, T. (eds) (1855) *The natural history of Pliny*. Translated by J. Bostock and H. T. Reily. London: Taylor and Francis.

Fujihara, T. (1926) 'Passivity of iron by dilute nitric acid', *Industrial & Engineering Chemistry*, 18(1), pp. 62–63. doi: 10.1021/ie50193a025.

Gadsden, J. A. (1975) *Infrared Spectra of Minerals and Related Inorganic Compounds*. USA: Butterworth.

Gibbs, F. W. (1951) 'Robert Dossie (1717–1777) and the society of arts', *Annals of Science*, 7, pp. 149–172. doi: 10.1080/00033795100202311.

Giesicke, B. and Ruoss, M. (2000) 'In Honor of Friendship: Function, Meaning and Iconography in Civic Stained-Glass Donations in Switzerland and Southern Germany', in Butts, B., Lee Hendrix, and Wolf, S. C. (eds) *Painting on Light. Drawings and Stained Glass in the Age of Dürer and Holbein*. Los Angeles: The J. Paul Getty Trust, pp. 43–55.

Goebbert, D. J. *et al.* (2009) 'Infrared Spectroscopy of the Microhydrated Nitrate Ions NO3-(H2O)1−6', *The Journal of Physical Chemistry A*, 113(26), pp. 7584–7592. doi: 10.1021/jp9017103.

Goldstein, H. F. *et al.* (1990) 'Raman study of CuO single crystals', *Physical Review B*, 41(10), pp. 7192–7194. doi: 10.1103/PhysRevB.41.7192.

Grambow, B. (1992) 'Geochemical Approach to Glass Dissolution', in Clark, D. E. and Zoitos, B. K. (eds) *Corrosion of Glass, Ceramics and Ceramics Superconductors: Principles, Testing, Characterization, and Applications*. New Jersey: Noyes Publications, pp. 124–152.

Gratuze, B. *et al.* (1992) 'De l'origine du cobalt dans les verres', *Revue d'Archéométrie*. Pôle éditorial archéologique de l'Ouest, Laboratoire d'archéométrie, 16, pp. 97–108. doi: 10.3406/arsci.1992.895.

Gratuze, B. *et al.* (1996) 'De l'origine du cobalt : du verre à la céramique', *Revue d'Archéométrie*, 20, pp. 77–94. doi: 10.3406/arsci.1996.939.

Grieb, H. (2004) 'Theophilus and the shrine of Vitus - A goldsmith's technique in the mirror of ancient references', *Metals 2004*, pp. 443–452.

Hagemann, H. *et al.* (1990) 'Raman spectra of single crystal CuO', *Solid State Communications*, 73(6), pp. 447–451.

Hasler, R. and Trümpler, S. (1998) 'Le vitrail suisse aux XVIe et XVIIe siècles', in *L'art du peintre-verrier*. Bourges: Le Parvis des Métiers, pp. 31–33.

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

Helwig, K. (2007) 'Iron oxide pigments, natural and synthetic', in Barbara H. Berrie (ed.) *Artists's Pigments, a Handbook of their History and Characteristics, vol. 4*. London: Archetype Publications Ltd., pp. 39–109.

Hess, D. (2000) 'In Search of Luís Alemão, Stained Glass in Germany from 1400 until 1460 and the fragments in Batalha', in *O Vitral - História, Conservação e Restauro. Encontro Internacional Mosteiro da Batalha, 27-29 de Abril de 1995*. Lisboa: IPPAR – Instituto Português do Património Arquitectónico, pp. 44–53.

Holbach (1752) *Art de la Verrerie, de Neri, Merret et Kunckel*. Paris: De l'imprimerie deJ. Chardon.

Hunt, L. B. (1976) 'The true story of Purple of Cassius', *Gold Bulletin*, 9(4), pp. 134–139. doi: 10.1007/BF03215423.

Jackson, C. M., Booth, C. A. and Smedley, J. W. (2005) 'Glass by design? Raw materials, recipes and compositional data', *Archaeometry*, 47(4), pp. 781–795.

Jackson, C. M. and Smedley, J. W. (2008) 'Theophilus and the Use of Beech Ash as a Glassmaking Alkali', in *Archaeology, History and Science: Integrating Approaches to Ancient Materials*, pp. 117–130.

Jembrih-Simbürger, D. *et al.* (2002) 'The colour of silver stained glass—analytical investigations carried out with XRF, SEM/EDX, TEM, and IBA', *J. Anal. At. Spectrom.*, 17(4), pp. 321–328. doi: 10.1039/B111024C.

Jonynaite, D. *et al.* (2009) 'XRD characterization of cobalt-based historical pigments and glazes', *Chemija*, 20(1), pp. 10–18.

Jorge, V. F. (ed.) (1984) *As Diversas Artes*. Translated by M. F. M. Cordeiro. Lisboa: Special offprint of Boletim Cultural da Assembleia Distrital de Lisboa, 89, vol. 1, 1983.

Jorge, V. F. (1989) *António de Pisa e a sua Memoria sobre vitral*. Boletim Cultural da Assembleia Distrital de Lisboa.

Kerssenbrock-Krosigk, D. Von (2008) *Glass of the Alchemists: Lead Crystal- Gold Ruby, 1650-1750*.

New York: Corning Museum of Glass.

Kunckel, J. (1752) ‘Art de la verrerie’, in *Art de la verreri, de Neri, Merret et Kunckel*. Paris: Chez Durand et chez Pissot.

Lautier, C. and Sandron, D. (eds) (2008) *Antoine de Pise, l’art du vitrail vers 1400*. France: Comité des travaux historiques et scientifiques.

Legodi, M. A. (2008) *Raman Spectroscopy applied to Iron Oxide Pigments from Waste Materials and Earthenware Archaeological objects*. University of Pretoria.

Legodi, M. A. and de Waal, D. (2007) ‘Raman spectroscopic study of ancient South African domestic clay pottery’, *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 66(1), pp. 135–142. doi: 10.1016/j.saa.2006.02.059.

Lehmann, H. (1941) *Geschichte der Luzerner Glasmalerei von den Anfängen bis zu Beginn des 18. Jahrhunderts*. Luzern: Keller & Co.

Lightbown, R. W. and Caiger-Smith, A. (eds) (1980) *Three Books of the Potter’s Art*. London: Scolar Press.

Louro, S. (2017) *O Vitral e as suas tintas: Grisalha e Amarelo de Prata*. Universidade NOVA de Lisboa.

Machado, A. *et al.* (2017) ‘Swiss Stained-Glass Panels: An Analytical Study’, *Microscopy and Microanalysis*, 23(04), pp. 878–890. doi: 10.1017/S1431927617000629.

Machado, A., Redol, P. and Branco, L. (2011) ‘Ionic liquids for medieval stained glass cleaning: a new frontier’, in *ICOM-CC Lisbon 2011: Sixteenth Triennial Conference*, pp. 1–9.

Machado, C. (2016) *Estudo de Produção de Grisalhas Históricas*. Universidade NOVA de Lisboa.

Marschner, H. (1996) ‘Analyses de pigments de grisaille sur des vitraux Munichois de l’église du Sain-Saveur, réalisés vers 1500’, in Wallonne, C. royale des monuments sites et fouilles de la R. (ed.) *Grisaille, Jaune d’argent, Sanguine, Email et Peinture à Froid, techniques et conservation. Forum pour la Conservation et la Restauration des Vitraux, Liège, 19-22 Juin 1996*. Liège: Commission royale des monuments, sites et fouilles, pp. 53–59.

Marshall, J. L. and

Marshall, V. R. (2005) ‘Rediscovery of the Elements - Agricola’, *The Hexagon*, 96(3), pp. 58–61.

Martinho, B. and Vilarigues, M. (2011) *Vitrais e Vidros, um gosto de D. Fernando II / Stained Glass and Glass Objects, Ferdinand II’s passion*. Edited by A. O. Martins. Parques de Sintra, Monte da Lua, S.A.

Martinho, B. and Vilarigues, M. (2012) ‘The Glass collection of King Ferdinand II of Portugal - Assembling the puzzle’, in *AIHV Annales du 19e congrès pour l’Histoire du Verre*. Piran, Eslovenia.

Mauck, A. (2012) ‘“By Merit Raised to That Bad Eminence”: Christopher Merrett, Artisanal Knowledge, and Professional Reform in Restoration London’, *Medical History*, 56(01), pp. 26–47. doi: 10.1017/S0025727300000260.

Merrett, C. (1662) *The Art of Glass*. London: A. W. for Octavian Pulleyn.

Merrifield, M. (1849a) *Original treatises dating from the XIIth to XVIIth centuries, on the arts of painting, in oil, miniature, mosaic, and on glass; of gilding, dyeing, and the preparation of colours and artificial gems, volume I*. London: John Murray.

Merrifield, M. (1849b) *Original treatises dating from the XIIth to XVIIth centuries, on the arts of painting, in oil, miniature, mosaic, and on glass; of gilding, dyeing, and the preparation of colours and artificial gems, volume II*. London: John Murray.

Milanesi, G. (ed.) (1864) *Dell'Arte del Vetro per Musaico, Tre Trattatelli dei Secoli XIV e XV ora per la prima volta publicati*. Bologna: Gaetano Romagnoli.

Misra, M. K., Ragland, K. W. and Baker, A. J. (1993) 'Wood ash composition as a function of furnace temperature', *Biomass and Bioenergy*, 4(2), pp. 103–116.

Moretti, C. and Hreglich, S. (2013) 'Raw Materials, Recipes and Procedures used for Glass Making', in Janssens, K. (ed.) *Modern Methods for Analysing Archaeological and Historical Glass*. West Sussex: John Wiley & Sons, Ltd, pp. 23–47.

Moretti, C. and Toninato, T. (2001) *Ricette vetrarie del Rinascimento*. Venezia: Marsilio Editori.

Navarro, J. M. F. (2003) *El Vidrio*. Madrid: Consejo Superior de Investigaciones Científicas.

Neven, S. (2014) 'Transmission of Alchemical and Artistic Knowledge in German Mediaeval and Premodern Recipe Books', in Sven Dupré (ed.) *Laboratories of Art, Alchemy and Art Technology from Antiquity to the 18th Century*. Switzerland: Springer International Publishing.

Pereira, P. (1990) *A Obra Silvestre e a Esfera do Rei - Iconologia da Arquitectura Manuelina na Grande Estremadura*. Coimbra: Instituto de História da Arte da Faculdade de Letras da Universidade de Coimbra.

Pereira, P. *et al.* (2007) *História da Arte Portuguesa: o 'Modo' Gótico (séculos XIII-XV)*. Edited by P. Pereira. Lisboa: Círculo Leitores.

Picollo, M. *et al.* (2007) 'Modern White Pigments: their Identification by means of noninvasive ultraviolet, visible, and infrared Fiber Optic Reflectance Spectroscopy', in Learner, T. J. S. et al. (eds) *Modern Paints Uncovered*. Los Angeles: The Getty Conservation Instiute, pp. 118–128.

Pradell, T. *et al.* (2016) 'Materials, Techniques, and Conservation of Historic Stained Glass "Grisailles"', *International Journal of Applied Glass Science*, 7(1), pp. 41–58. doi: 10.1111/ijag.12125.

Raguin, V. C. (2008) *The History of Stained Glass, the Art of Light to medieval contemporary*. London: Thames & Hudson Ltd.

Reboulleau and Magnier (1866) *Nouveau Manuel Complet de la Peinture sur Verre, sur Porcelaine & sur Émail, des Émaillages Industriels et de la fabrication des Émaux et des Couleurs Vitrifiables*. Paris: Librairie Encyclopédique de Roret.

Redol, P. (1995) 'O Mosteiro da Batalha e o Vitral em Portugal nos Séculos XV e XVI, contributos para o seu estudo', in IPPAR (ed.) *O Vitral - História, Conservação e Restauro*. Lisboa: Publimpressores - Artes Gráficas Lda., pp. 12–43.

Redol, P. (2003) *O Mosteiro da Batalha e o Vitral em Portugal nos séculos XV e XVI*. Batalha: Câmara Municipal da Batalha.

Rehren, T. and Freestone, I. C. (2015) 'Ancient glass: from kaleidoscope to crystal ball', *Journal of Archaeological Science*, 56, pp. 233–241. doi: 10.1016/j.jas.2015.02.021.

Robinet, L. *et al.* (2011) 'Investigation of the Discoloration of Smalt Pigment in Historic Paintings by Micro-X-ray Absorption Spectroscopy at the Co K-Edge', *Analytical Chemistry*, 83(13), pp. 5145–5152. doi: 10.1021/ac200184f.

Robinet, L., Bouquillon, A. and Hartwig, J. (2008) 'Correlations between Raman parameters and elemental composition in lead and lead alkali silicate glasses', *Journal of Raman Spectroscopy*, 39, pp. 618–626. doi: 10.1002/jrs.1894.

Robinet, L., Spring, M. and Pagès-Camagna, S. (2013) 'Vibrational spectroscopy correlated with elemental analysis for the investigation of smalt pigment and its alteration in paintings', *Analytical Methods*, 5(18), pp. 4628–4638. doi: 10.1039/c3ay40906f.

Rodrigues, A. *et al.* (2013) 'The Stained-glass Collection of King Ferdinand II of Portugal: Concept, Conservation, and Chemical Analysis of Two Panels', in Roemich, H. and Campagne, K. van L. (eds) *Recent Advances in Glass, Stained Glass and Ceramics Conservation, ICOM-CC Working Group Glass and Ceramics Interim Meeting and Forum of the International Scientific Committee for the Conservation of Stained Glass (Corpus Vitrearum-ICOMOS)*. Amsterdam: Spa Uitgevers, pp. 259–267.

Rodrigues, A. *et al.* (2014) 'Fungal biodeterioration of stained-glass windows', *International Biodeterioration & Biodegradation*, 90, pp. 152–160. doi: 10.1016/j.ibiod.2014.03.007.

Rodrigues, A. and Martinho, B. (2015) 'The Assemblage of a Distinct Glass Collection: The creation and display of the glass and stained-glass collection of Ferdinand II of Portugal', in *COLLECTING THROUGH CONNECTIONS: GLASS AND STAINED-GLASS COLLECTORS AND HEIR NETWORKS IN THE 19TH CENTURY*. Instituto de História da Arte, pp. 76–93.

Sanderson, D. C. W. and Hunter, J. R. (1981) 'Composition variability in vegetable ash', *Science and Archaeology*, 23, pp. 27–30.

Santos, Â. and Vilarigues, M. (2018) 'Sanguine paint: production, characterization, and adhesion to the glass substrate', *Studies in Conservation*. doi: 10.1080/00393630.2018.1482708.

Schalm, O. (2000) *Characterization of paint layers in stained-glass Windows: main causes of the degradation of nineteenth century grisaille paint layers.* Faculteit wetenschappen, Universiteit Antwerpen.

Schalm, O. *et al.* (2007) 'Composition of 12–18th century window glass in Belgium: Non-figurative windows in secular buildings and stained-glass windows in religious buildings', *Spectrochimica Acta Part B*, 62, pp. 663–668. doi: 10.1016/j.sab.2007.03.006.

Schalm, O. *et al.* (2009) 'Enamels in stained glass windows: Preparation, chemical composition, microstructure and causes of deterioration', *Spectrochimica Acta Part B: Atomic Spectroscopy*. Elsevier B.V., 64(8), pp. 812–820. doi: 10.1016/j.sab.2009.06.005.

Schalm, O., Janssens, K., F. Adams, Albert, J., Peeters, K., & Caen, J. (1996). Une étude historique et chimique de peinture de verre "rouge Jean Cousin." In C. royale des monuments sites et fouilles de la R. Wallonne (Ed.), Grisaille, Jaune d'argent, Sanguine, Email et Peinture à Froid, techniques et conservation. Forum pour la Conservation et la Restauration des Vitraux, Liège, 19-22 Juin 1996 (pp. 155–162). Liège: Commission royale des monuments, sites et fouilles.

Schneider, J. (1971) *Glasgemälde. Katalog der Sammlung des Schwezerischen Landesmuseums Zürich*. Edited by T. Gut. Stäfa.

Schneider, J. (1978) 'Glasgemälde : Neuerwerbungen 1978', *Jahresbericht, Schweizerisches Landesmuseum Zürich*, 87. doi: 10.5169/seals-395350.

Schwertmann, U. and R. M. Cornell (2000) *Iron Oxides in the Laboratory, Preparation and Characterization*. 2nd edn. Weinheim: WILEY-VCH Verlag GmbH & Co.

Shelby, J. E. (1997) *Introduction to glass science and technology*. Cambridge: The Royal Society of Chemistry.

Smedley, J. W., Jackson, C. M. and Booth, C. A. (1998) 'Back to the roots: the raw materials, glass recipes and glassmaking practices of Theophilus', in McCray, P. and Kingery, W. D. (eds) *The prehistory and history of glass and glassmaking technology. Ceramics and Civilization, vol. III*. Westerville, OH: American Ceramic Society, pp. 145–165.

Smith, C. S. (1940) 'Biringuccio's "Pirotechnia" - a neglected Italian metallurgical classic', *Mining and Metallurgy*, pp. 189–192.

Smith, C. S. and Gnudi, M. T. (eds) (1943) *The Pirotechnia of Vanoccio Biringuccio. The Classic sixteenth-century treatise on metals and metallurgy*. Translated by C. S. Smith and M. T. Gnudi. New

York, United States: Dover Publications, Inc.

Smith, C. S. and Hawthorne, J. G. (1974) 'Mappae Clavicula: A Little Key to the World of Medieval Techniques', *Transactions of the American Philosophical Society*, 64(4). doi: 10.2307/1006317.

Smith, P. H. (2008) 'Alchemy as the Imitator of Nature', in *Glass of the Alchemists: Lead Crystal-Gold Ruby, 1650-1750*. New York: Corning Museum of Glass.

Van der Snickt, G. *et al.* (2006) 'Blue Enamel on Sixteenth - and Seventeenth-Century Window Glass', *Studies in Conservation*, 51(2), pp. 212–22. doi: 10.2307/20619450.

Stern, W. B. and Gerber, Y. (2004) 'Potassium-calcium glass: new data and experiments', *Archaeometry*, 46(1), pp. 137–156.

Stern, W. and Gerber, Y. (2009) 'Ancient potassium-calcium glass and its raw materials (wood-ash, fern-ash, potash) in Central Europe', *Mitteilungen der Naturforschenden Gesellschaften beider Basel*, 11, pp. 107–122.

Strobl, S. (1990) *Glastechnik des Mittelalters*. A. Gentner.

Thompson, D. V. (ed.) (1954) *The Crafstmann Handbook 'Il Libro dell'Arte' Cennino d'Andrea Cennini*. Translated by D. V. Thompson. New York, United States: Dover Publications, Inc.

Treeck, P. van (2000) 'On the Artistic Technique of Glass Painting in the Age of Dürer and Holbein and Its Conservation Problems', in Butts, B., Hendrix, L., and Wolf, S. C. (eds) *Painting on Light. Drawings and Stained Glass in the Age of Dürer and Holbein*. Los Angeles: The J. Paul Getty Trust, pp. 57–65.

Trengove, L. (1965) 'Chemistry at the Royal Society of London in the eighteenth century—III(B)—metals', *Annals of Science*, 21(3), pp. 175–201. doi: 10.1080/00033796500200111.

Turner, W. E. S. (1956) 'Studies in ancient glasses and glassmaking processes. Part V. Raw materials and melting processes', *Journal of the Society of Glass Technology*, 40, pp. 277–300.

Turner, W. E. S. (1963) 'The tercentenary of Neri-Merrett's The Art of Glass', *Advances in Glass Technology*, 2, pp. 181–201.

Verità, M. (1996) 'Composition, structure et mecanisme de detérioration des grisailles', in Wallonne, C. royale des monuments sites et fouilles de la R. (ed.) *Grisaille, Jaune d'argent, Sanguine, Email et Peinture à Froid, techniques et conservation. Forum pour la Conservation et la Restauration des Vitraux, Liège, 19-22 Juin 1996*. Liège: Commission royale des monuments, sites et fouilles, pp. 61–68.

Vieil, P. Le (1774) *L'Art de la peinture sur verre et de vitrerie*. Paris: De l'imprimerie de L. F. Delatour.

Vilarigues, M. (2008) *Estudo do Efeito da Adição de Iões Metálicos na Corrosão de Vidros Potássicos*. Universidade NOVA de Lisboa.

Vilarigues, M. *et al.* (2009) 'Stained glasses under the nuclear microprobe: A window into history', *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*. Elsevier B.V., 267(12–13), pp. 2260–2264. doi: 10.1016/j.nimb.2009.03.049.

Vilarigues, M. *et al.* (2011) 'Corrosion of 15th and early 16th century stained glass from the monastery of Batalha studied with external ion beam', *Materials Characterization*. Elsevier Inc., 62(2), pp. 211–217. doi: 10.1016/j.matchar.2010.12.001.

Vilarigues, M., Delgado, J. and Redol, P. (2011) 'Stained Glass from the Convent of Christ in Tomar, Portugal: History and Characterization', *Journal of glass studies*, 53, pp. 246–251.

Vilarigues, M. and Da Silva, R. C. (2004) 'Ion beam and Infrared analysis of medieval stained glass', *Applied Physics A: Materials Science and Processing*, 79, pp. 373–378. doi: 10.1007/s00339-004-2538-9.

Vilarigues, M. and da Silva, R. C. (2006) ‘Characterization of potash-glass corrosion in aqueous solution by ion beam and IR spectroscopy’, *Journal of Non-Crystalline Solids*, 352(50–51), pp. 5368–5375. doi: 10.1016/j.jnoncrysol.2006.08.032.

Vilarigues, M. and da Silva, R. C. (2009) ‘The effect of Mn, Fe and Cu ions on potash-glass corrosion’, *Journal of Non-Crystalline Solids*. Elsevier B.V., 355(31–33), pp. 1630–1637. doi: 10.1016/j.jnoncrysol.2009.05.051.

de Waal, D. (2009) ‘Micro-Raman and portable raman spectroscopic investigation of blue pigments in selected Delft plates (17-20th century)’, *Journal of Raman Spectroscopy*, 40(12), pp. 2162–2170. doi: 10.1002/jrs.2389.

Weber, B. *et al.* (2011) ‘Crystal Structure of Iron(II) Acetate’, *Zeitschrift für anorganische und allgemeine Chemie*, 637(1), pp. 102–107. doi: 10.1002/zaac.201000274.

Wedepohl, K. H. and Simon, K. (2010) ‘The chemical composition of medieval wood ash glass from Central Europe’, *Chemie der Erde - Geochemistry*. Elsevier, 70(1), pp. 89–97. doi: 10.1016/j.chemer.2009.12.006.

Zecchin, L. (1964) ‘Le ricette vetrarie di Montpellier’, *Journal of glass studies*, X, pp. 75–82.

Zecchin, L. (1987) ‘Le ricette vetrarie di Montpellier’, in *Vetro e Vetrai di Murano*. Venezia: Arsenale Editrice s. r. l., pp. 247–276.

de Waal, D. (2009) ‘Micro-Raman and portable raman spectroscopic investigation of blue pigments in selected Delft plates (17-20th century)’, *Journal of Raman Spectroscopy*, 40(12), pp. 2162–2170.

Wedepohl, K. H. and Simon, K. (2010) ‘The chemical composition of medieval wood ash glass from Central Europe’, *Chemie der Erde - Geochemistry*. Elsevier, 70(1), pp. 89–97.

Zecchin, L. (1964) ‘Le ricette vetrarie di Montpellier’, *Journal of glass studies*, X, pp. 75–82.

Zecchin, L. (1987) ‘Le ricette vetrarie di Montpellier’, in *Vetro e Vetrai di Murano*. Venezia: Arsenale Editrice s. r. l., pp. 247–276.

APPENDIX I

ANALYTICAL TECHNIQUES USED IN THE CHARACTERIZATION OF GLASS PAINTING TECHNIQUES.

Blue enamels, sanguine and grisaille paints, both the reproduced samples and case studies, were morphological and chemically characterized. The present chapter contains a brief description of the main analytical techniques used in this study – Optical microscopy (OM), Scanning Electron Microscopy (SEM), Fibre Optics Reflectance Spectroscopy (FORS), X-ray Diffraction (XRD), Raman Spectroscopy, Fourier Transform Infrared Spectrometry (FTIR), micro-Particle Induce X-ray Emission (μ-PIXE), and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Occasionally, micro-Energy Dispersive X-ray Spectroscopy (μ-EDXRF), Inductively coupled plasma mass spectrometry (ICP-MS), and pH analysis were performed.

I.1. Optical Microscopy

Optical microscopy is a useful tool for a first assessment of the overall morphology of the paint layers. Corrosion deposits, fissures, and detachments of the paint layers are thus possible to see with the use of this technique. Dark and bright field were the two light filters mainly used. The dark field allows the perception of surface details which are not visible with a bright field, since the illumination is oblique in relation with the surface (Vilarigues, 2008).

Blue enamel powder samples were also characterized by optical microscopy. Samples were carefully examined under a magnifier in order to evaluate their size and select samples to prepare the dispersions. The dispersions were examined by transmitted light optical microscopy, under plane and cross polarised light.

The equipment used was an Axioplan 2® Zeiss microscope, Zeiss with a Nikon DMX digital camera. The microscope is equipped with light illuminator (tungsten halogen light source, HAL 100) and a digital Nikon camera DXM1200F, with Nikon ACT-1 application program software, for micrographs. The scales for all objectives were calibrated within the Nikon ACT-1 software.

The equipment is located at the Department of Conservation and Restoration from FCT-UNL.

I.2. Scanning Electron Microscopy with X-ray microanalysis (SEM-EDS)

Scanning electron microscopy is a valuable resource to analyse glass samples with a greater detail when compared to optical microscopy. SEM equipped with an energy dispersive spectroscopy detector (EDS)

produces higher resolution images, which enables the morphological characteristics of the samples to be highlighted (Janssens, 2013). X-ray elemental maps are also very useful especially for heterogeneous surfaces such as glass paintings. Backscattered imaging (BSE) allows visualizing the main differences on the composition of the surface to be analysed.

In the present study, both glass paint reproductions and stained-glass samples were analysed by SEM-EDS with BSE imaging. In the case of the reproduced painted samples after corrosion, both surface and cross-section were analysed.

For the case studies, two different types of equipment were used. The stained-glass samples from VCR set were analysed by SEM-EDS at the Geosciences Department at the University of Fribourg. The equipment used was a Philips® FEI XL30 Sirion FEG scanning electron microscope, operated at a beam acceleration voltage of 20 kV and a beam current of 5 nA. A backscattered electron detector was used for imaging. X-ray maps were collected using an energy-dispersive X-ray spectrometry system from EDAX. The equipment was operated by Ildiko Katona-Serneels.

The samples from the collections of Batalha Monastery, Tomar, and Pena National Palace and the glass paint reproductions were analysed at the MicroLab Electron Microscopy Laboratory, at Instituto Superior Técnico (IST) in Lisbon. The equipment used was a FEG-SEM from JEOL, model JSM7001F, operating at a beam acceleration voltage of 20 kV, using a backscattered electron detector for imaging. X-ray maps were collected using an INCA 250 energy-dispersive X-ray spectrometer system from Oxford Instruments. The equipment was operated by Isabel Dias Nogueira.

I.3. Fibre Optics Reflectance Spectroscopy (FORS)

This technique is acknowledged for being portable, performing non-invasive and quick analysis. The first use of non-invasive spectroscopic techniques for colour analysis was made in the seventies at the National Gallery and Victoria and Albert Museum in London. The first non-invasive spectroscopic analyses of stained-glass windows *in situ* using FORS were made by the research group of the Institute of Applied Physics “Nello Carrara”, Florence (Bacci and Picollo, 1996; Bacci *et al.*, 2007).

Cobalt, iron and copper are the main colouring ions responsible for the colour of blue enamels, sanguine red and grisaille. Table 4.1 presents their respective oxidation state, absorption bands and electronic transitions.

In this study, this equipment was used for the colour characterization of the glass paint reproductions, both powder and paint samples, and also to stained-glass panels case study.

The equipment used is located at the Department of Conservation and Restoration from FCT-UNL. A MAYA 200 PRO from Ocean Optics spectrophotometer with a single beam dispersive optic fibre was used, together with a 2048 CCD Si detector that allows operating in the 200-1050 nm range. The light source is an HL-200-HP 20-watt halogen from Ocean Optics, with a single optical path between 360-

2500 nm. The spectra were acquired in reflectance (R) mode, with a 45°/45° configuration (illumination angle/acquisition) and ca. 2 mm of diameter of analysed area. Spectra were obtained between 360-1050 nm, with an integration time of 8 ms with 15 average scans. A Spectralon® surface was used as a reference. For the glass paint powders, a sample was placed between two glass plates and analysed over the Spectralon® surface. The calibration for this procedure was performed with a glass plate over the Spectralon® surface in order to acquire the contribution of the glass plate. For the glass paints, the optic fibre was placed directly over the enamel surface and analysed over the Spectralon® surface. Three measurements were taken for each sample, presenting as a final result the average spectra of these three measurements, to which was applied the Kubelka-Munk formula[1]. CIELab measurements were acquired simultaneously, using the D65 illuminant standard and the 10° observer. Measurements were taken on each enamel sample. In addition Lab* and *xy* coordinates were calculated from an average of three measurements of each sample.

FORS spectra were also acquired on blue enamel paints present in stained-glass windows located at Pena National Palace. Stained glass windows are presented in their original wood frame. Therefore, acquisition spectra were taken in the vertical, placing the optic fibre with a 45°/45° configuration with the glass surface. In the panels PNP2808, Heraldic Panel with the coat of arms of the canton Luzern, PNP2820, Ioannes Henricvs Fleischlin, and PNP2858, *Saint Andre, Saint Peter and Saint Paul*, enamel painting is placed on the exterior side; hence the acquisition performed took into account the contribution of the glass. For the panel PNP2855, *The Last Supper*, the analysis was performed directly on the enamel paint. The light placed behind the windows was shut down, in order to annul its interference with the acquisition. CIELab measurements were acquired simultaneously using the same parameters previously mentioned.

I.4. X-ray Diffraction (XRD)

X-ray diffraction analysis of glass objects is suitable to identify crystalline phases present on the glass, either as microcrystals in the silica network or in the corrosion layers (Navarro, 2003).

In this study, XRD analysis was helpful to identify the presence of crystalline phases on the glass paints, before and after corrosion studies, and to characterize sanguine and grisaille powder samples.

The analyses were performed at the associated laboratory for green chemistry (REQUIMTE/LAQV) from the Chemistry Department of FCT-UNL. A Benchtop X-Ray Diffractometer RIGAKU model MiniFlex II, with a Cu Kα, 30 kV, and 15 mA was used. The spectra were acquired at 2 °/min. The

[1] The Kubelka-Munk formula, $F(R_\infty)=(1-R_\infty)2/2R_\infty=K/S$, relates the diffuse reflectance R_∞ with the ratio K/S, being K the absorption and S the scattering coefficients. The function $F(R_\infty)$ can be linear with the concentration of the absorbing component, providing that the scattering coefficient is independent of the concentration. The application of the Kubelka-Munk formula is a good approach to determine the absorbance from the diffuse reflectance (Bacci *et al.*, 2003; Soares, 2014).

RUFF database and related published work were used for comparison purposes. The equipment was operated by Nuno Costa.

I.5. Micro-Raman Spectroscopy (µ-Raman)

Raman is a form of vibrational spectroscopy which measures the interaction between photons (or neutrons) and the low energy level of the analysed materials, meaning vibration levels (Colomban, 2013). Alongside with infrared analysis, Raman spectroscopy allows to characterize a material on a molecular level. Its utility on the characterization of glass, enamels and glazes is highly recognized and extensive (e.g. Coentro *et al.*, 2012; Caggiani *et al.*, 2013; Colomban, 2013; Coutinho *et al.*, 2014; Colomban, Arberet and Kırmızı, 2017). It is acknowledge for performing analyses with minimal or no sampling preparation, being also possible to perform *in situ* analyses (Colomban, Arberet and Kırmızı, 2017).

For the present study, µ-Raman analyses were performed on blue enamel paint and sanguine red paint reproductions. A Labram 300 Jobin Yvon spectrometer, equipped with a He-Ne laser of 500 mW power operating at 785 nm and a solid-state laser of 500 mW power operating at 532 nm was used, located at the Department of Conservation and Restoration from FCT-UNL. The laser beam was focused either with 50x or 100x Olympus objective lenses. The laser power at the surface of the samples was controlled using a set of neutral density filters varying between 0.1 and 1.7 mW. A mixed Gaussian-Lorentzian curve-fit provided by the LabSpec software (v 5.15.25) was used to determine the exact peak wavenumbers.

I.6. Fourier Transform Infrared Spectrometry (FTIR)

Most commonly used for the characterization of organic materials, infrared spectroscopy is also used for the identification of inorganic materials. The absorption bands are broader when compared with organic compounds, and are situated at lower wavenumbers (Derrick, 1999).

For the present study, FTIR was used for the chemical characterization of blue enamel powder samples, before and after corrosion process, and for sanguine red powder samples.

The equipment used is located at the Department of Conservation and Restoration from FCT-UNL. Infrared analyses were made using a Nicolet Nexus spectrophotometer. The spectra were collected in transmission mode, between 4000 – 400 cm^{-1}, with a resolution of 4 cm^{-1} and 64 scans, using KBr pellets. Preparation of KBr pellets involved mixing and grinding a small quantity of sample with KBr powder and then pressing it under high pressure (± 8.5 Newton/m^2). The spectra are shown in this work as acquired, without corrections or any further manipulations, except for the occasional removal of the CO_2 absorption at ca. 2300–2400 cm^{-1}.

I.7. Micro-Particle Induced X-ray Emission (μ-PIXE)

PIXE analyses have been widely used for the study of the chemical composition of glass (Šmit *et al.*, 2002, 2005; Coutinho *et al.*, 2016). By using an internal ion-beam in a vacuum, important low Z elements such as sodium and aluminium are also detectable (Šmit, 2013). This technique does not leave any undesirable alterations to the glass, unlike other analytical techniques such as ICP-MS, which can leave craters of ca. 100 μm in diameter. It has a very high sensitivity, allowing for trace and ultra-trace elemental analysis (Calligaro, 2008). In addition, PIXE can perform analysis of selected areas of very small size, which can be important for the determination of the chemical composition of heterogeneous surfaces, for example, of grisaille and enamels.

The ion beam analytical facilities at IST, Pólo de Loures, were used. They comprise a 2.5 MV Van de Graaff accelerator and an OM150 Oxford Microbeam scanning nuclear microprobe. The stained-glass fragments embedded in resin were irradiated with focused proton beams (down to 3x4 μm2) in a vacuum. A 145 eV resolution SDD X-ray detector was used to obtain sample X-ray spectra. With the microprobe beam scanning system, elemental distribution maps were obtained and specific regions of interest selected for quantitative analysis. The samples were irradiated both with a 1 MeV proton beam (no filter) to obtain concentrations of Na, Mg, and Al and with a 2 MeV proton beam (using a 50 μm Mylar filter in front of the X-ray detector) for trace element quantification (for elements heavier than Fe). Operation and basic data manipulation were achieved using OMDAQ software (Grime and Dawson, 1995); quantitative analysis was done with the GUPIX program (Campbell *et al.*, 2010).
The results - the given weight percentage of the element oxide - were normalized to 100%. The trace element concentrations analysed at 2 MeV were normalized to the iron content (Bellot-Gurlet *et al.*, 2005). When determining the base glass composition of the coloured glass, the colouring elements (e.g. Cu, Co, Mn) were removed from the data set and again normalized to 100%.
Glass reference standards from the Corning Museum of Glass were also analysed (CMOG B and CMOG C). The parameters used to obtain their respective concentration were used to determine the final composition of the stained glass samples.
For the analysis of powder samples, tablets of each sample were prepared and placed over a carbon tape, to be analysed with an external ion beam. For the analysis of painting samples, polished cross-sections of all of the samples were prepared by cutting a small piece of approximately 5 mm of each sample and mounting it in epoxy resin (Araldite2020®). The equipment was operated by Luis Cerqueira Alves.

I.8. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

The use of ICP-AES to assess the chemical composition of glass requires the dissolution of the sample and therefore is not considered when other analytical techniques such as LA-ICP-MS or μ-PIXE are available, however, it can be considered a good approach when submitting the enamel powder samples

to accelerated weathering by placing the samples in water. Since it is expected an ion exchange between glass and water, ICP-AES is a good approach to determine major and minor elements present in the solution.

For the present study, ICP-AES analyses were used for the characterization of the blue enamel powder samples after the corrosion process, by measuring the elemental composition of the solution.
The equipment used is located at the associated laboratory for green chemistry (REQUIMTE/LAQV) from the Chemistry Department of FCT-UNL. An Horiba Jobin-Yvon Ultima model was used, equipped with a 40,68 MHz RF generator, Czerny-Turner monochromator with 1,00 m (sequential), and an autosampler AS500. The equipment was operated by Carla Rodrigues.

APPENDIX II

DIFRACTOGRAMS OF SKUTTERDITE (SAMPLE b), BEFORE AND AFTER CALCINATION

For the interpretation of the difractograms, RUFF database was accessed. The files used were the following: ID R100195, R040031, R061007, R080095, R061021, R060804 and R050650.

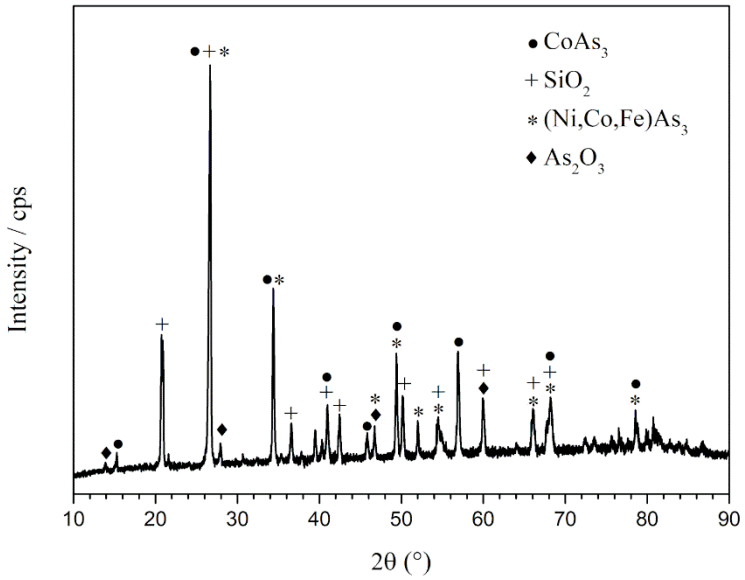


Figure II.1 – XRD pattern for the mineral skutterudite, sample b.

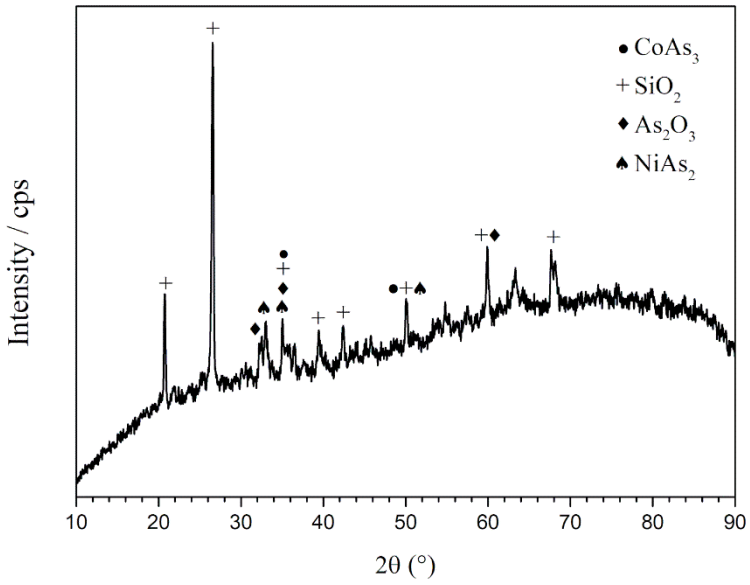


Figure II.2 – XRD pattern for the calcined mineral skutterudite, sample b.

APPENDIX III

PREPARATION OF THE BLUE ENAMEL RECIPES ACCORDING TO ROBERT DOSSIE'S *THE HANDMAID TO THE ARTS*

The preparation of the blue enamels was prepared according to the instructions given by Robert Dossie, meaning they were prepared into two steps: first the preparation of the base glasses, and then the preparation of the blue enamels. Regarding the bases glass containing lead glass, the preparation of the lead glass was performed prior to the preparation of the base glasses.
Table III.1 presents the composition used for the production of the base glasses, and table III.2 presents the composition used for the production of the blue enamels.

For all the blue enamels the following amounts were prepared:

1. Base glasses: 100 g;
2. Blue enamels: 50 g;
3. Glass of lead: 140 g;
4. Smalt glass: 100g (71 g SiO_2, 7 g CoO, 21 g K_2CO_3 and 1 g Al_2O_3);
5. Zaffer: mixture of SiO_2:CoO 2:1 (w:w).

Table III.1 – Composition used for the production of the base glasses (g).

	Pb_3O_4:SiO_2 2:1 (wt%)	*SiO_2*	*K_2CO_3*	*NaCl*	*$Na_2B_4O_7 \cdot 10H_2O$*	*As_2O_3*
Base glass 1	67		25	8		
Base glass 2	59		22		15	4
Base glass 3		64	24	8	4	
Base glass 4		57.1	14.3	7.14	14.3	7.14

Table III.2 – Composition used for the production of the blue enamels (g).

	Base glass	Zaffer	Smalt	Copper
R6B1Z R6B2Z	42.9	0.95 SiO2 + 0.47 CoO + 5.68 borax*		
R8B1Z R8B2Z R8B3Z R8B4Z	40	6.7 SiO_2 + 3.3 CoO		
R10B3Z R10B4Z	35.7	4.76 SiO_2 + 2.38 CoO		7.14
R6B1S R6B2S	42.9		1.42 smalt + 5.68 borax*	
R8B1S R8B2S R8B3S R8B4S	40		10	
R10B3S R10B4S	35.7		7.14	7.14

R: enamel recipe; B: base glass; S: smalt; Z: zaffer

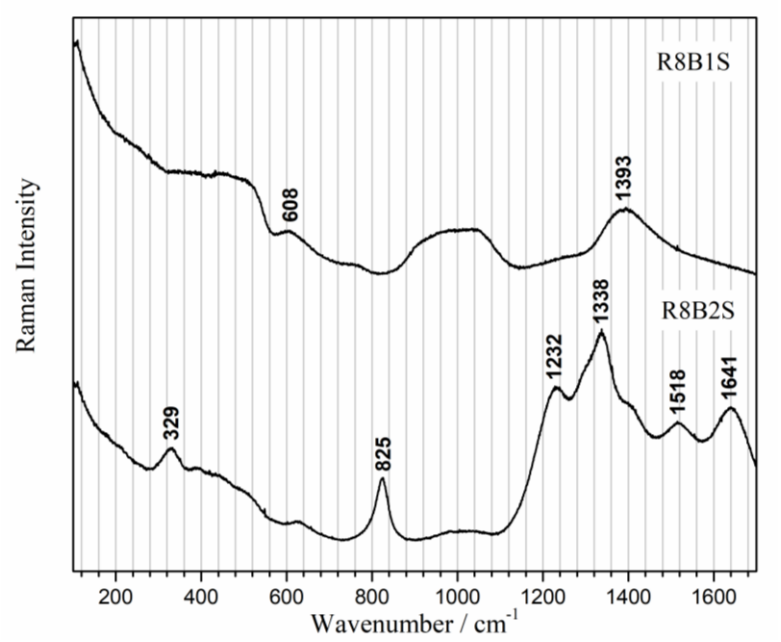
* For enamel recipes 6 the colouring agent was mixed with borax (cf. Figure 4.8, p. 51).

The List of the chemical reagents used, for the productions of the blue enamels both from Antonio Neri and Robert Dossie's recipes, is present below:

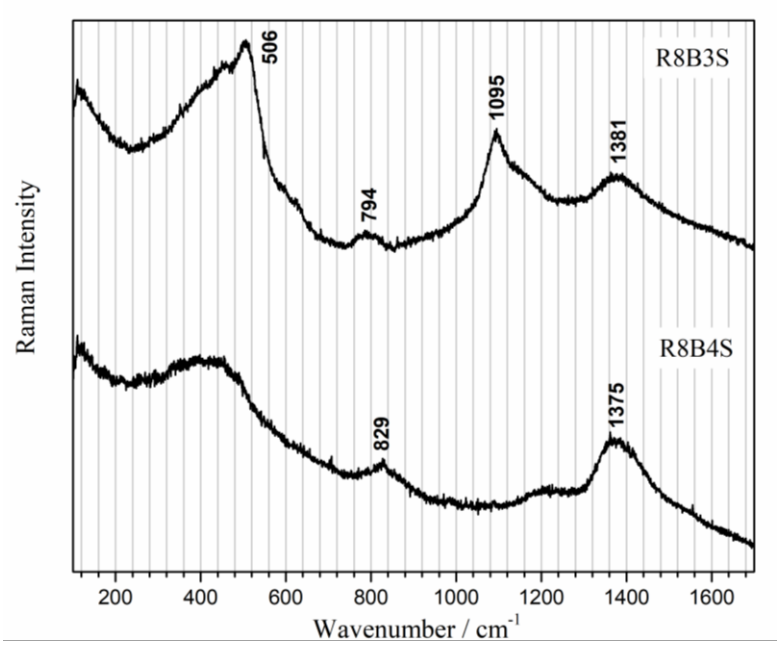
- Lead (II,IV) oxide, 99 % pure, CAS 1314-41-6.
- Silicon dioxide, purum p.a., Sigma-Aldrich®, CAS 14808-60-7.
- Potassium carbonate, ≥99 % pure, Sigma-Aldrich®, CAS 584-08-7.
- Sodium Chloride, 99.9 % pure, PanReac AppliChem®, CAS 7647-14-5.
- Sodium tetraborate decahydrate, 99.5 % pure, Riedel-de-Haën™, CAS 1303-96-4.
- Arsenic (III) oxide, 99 % pure, Sigma-Aldrich®, CAS 1327-53-3.
- Cobalt (II) oxide, 95 % pure, Alfa Aesar, CAS 1307-96-6.
- Aluminum oxide, ≥98 % pure, Sigma-Aldrich®, CAS 1344-28-1.
- Tin (IV) oxide, 99.9 % pure, Sigma-Aldrich®, CAS 18282-10-5.

APPENDIX IV

μ-RAMAN SPECTROSCOPY OF BLUE ENAMEL PAINT RECIPES R8, WITH SMALT AS COLOURING AGENT



(a)



(b)

Figure IV.1 – Raman spectra of (a) blue enamel recipes R8B1S and R8B2S, and (b) recipes R8B3S and R8B4S.

APPENDIX V

μ- PIXE RESULTS FOR THE BASE GLASS AND PAINT LAYERS FROM VCR AND PNP SETS (WT. %)

Table V.I - μ- PIXE results for the glass from VCR and PNP sets (wt. %).

Sample	Colour	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_5	Rb_2O	SrO	BaO	K_2O/CaO
VCR01	colourless	0.4	3.4	4.4	58.0	2.56	0.15	0.05	6.29	22.33	0.23	0.72	1.02	n.d.	<0.01	0.01	0.02	0.02	<0.01	0.06	0.26	0.28
VCR02	colourless	0.5	3.9	4.7	61.5	2.15	0.14	0.05	6.59	17.77	0.24	0.90	0.90	n.d.	n.d.	0.01	0.02	0.03	<0.01	0.06	0.47	0.37
VCR03	colourless	0.4	3.6	3.0	61.6	1.49	0.30	0.02	9.67	17.26	0.14	1.18	0.49	n.d.	n.d.	0.02	0.03	n.d.	<0.02	<0.04	0.69	0.56
VCR04	colourless	0.8	4.5	5.5	58.7	2.63	0.06	0.21	7.23	17.91	0.23	0.55	1.18	n.d.	n.d.	0.01	0.04	0.03	<0.01	<0.02	0.22	0.40
VCR05	colourless	0.5	3.9	4.7	62.0	2.16	0.14	0.05	6.48	17.42	0.21	0.86	0.88	n.d.	n.d.	0.01	0.02	0.03	<0.01	0.05	0.46	0.37
VCR06	colourless	8.3	0.8	1.9	68.5	0.28	0.57	0.42	2.78	15.33	0.11	0.11	0.35	n.d.	<0.01	0.003	0.01	0.02	<0.01	<0.01	0.02	0.18
VCR07	colourless	1.2	3.8	4.5	59.6	2.23	0.18	0.24	5.88	20.04	0.19	0.74	0.83	n.d.	n.d.	0.01	0.02	<0.01	<0.01	0.06	0.26	0.29
	red	1.1	3.7	4.6	59.3	2.24	<0.03	0.22	6.02	19.71	0.18	0.69	0.84	n.d.	n.d.	0.67	0.02	0.01	<0.01	0.07	0.28	0.31
VCR08	colourless	0.7	3.5	4.2	61.6	2.21	0.21	0.12	6.20	19.13	0.20	0.81	0.82	n.d.	0.01	0.01	0.02	0.01	<0.01	0.05	0.33	0.32
	red	0.7	3.5	4.3	61.2	2.15	0.21	0.09	6.41	19.34	0.19	0.79	0.87	n.d.	0.02	0.62	0.03	0.02	<0.01	0.05	0.33	0.33
VCR09	red	0.4	3.2	3.40	56.4	1.46	0.32	<0.01	11.58	18.79	0.15	2.79	0.48	<0.01	<0.01	0.01	0.02	<0.01	<0.01	0.08	0.75	0.62
	blue	0.4	3.4	3.2	58.6	1.47	0.30	<0.02	10.96	18.54	0.16	1.10	0.77	0.17	0.05	0.01	0.01	0.31	<0.01	0.05	0.49	0.59
VCR10	colourless	0.4	3.2	3.9	60.0	1.20	0.24	0.03	15.28	13.89	0.17	1.24	0.36	n.d.	n.d.	<0.01	0.02	<0.01	<0.01	0.10	0.43	1.10
	purple	0.5	3.3	3.9	57.4	1.21	0.30	0.03	14.88	14.30	0.20	2.94	0.55	0.02	0.01	0.01	0.02	0.03	<0.01	0.10	0.43	1.04
VCR11	colourless	2.9	3.0	2.9	62.5	2.72	0.11	0.59	3.38	19.74	0.13	0.52	0.56	n.d.	<0.01	0.02	0.03	<0.01	<0.01	0.07	0.09	0.17
VCR12	colourless	2.1	3.2	5.4	59.1	1.81	0.08	0.43	5.30	19.76	0.25	0.77	0.84	n.d.	0.01	0.01	0.03	0.03	<0.01	0.09	0.24	0.27
VCR13	colourless	2.7	2.9	2.9	62.7	2.80	0.10	0.60	3.37	19.73	0.16	0.51	0.53	n.d.	<0.01	0.02	0.03	<0.01	<0.01	0.07	0.09	0.17
VCR14	red layer	0.7	3.5	2.8	58.4	1.18	0.35	0.06	14.13	15.94	0.12	1.80	0.32	<0.01	<0.01	0.01	0.02	<0.01	<0.01	0.11	0.57	0.89
	blue layer	0.6	3.5	2.7	58.3	1.22	0.33	0.06	14.03	15.91	0.11	1.77	0.43	0.08	0.02	0.01	0.02	0.41	<0.01	0.08	0.43	0.88
VCR15	red layer	0.7	3.5	2.9	58.8	1.19	0.38	0.06	14.13	15.92	0.11	1.76	0.28	<0.01	0.01	0.01	0.02	<0.01	0.02	0.09	0.49	0.89
	blue layer	0.7	3.6	2.7	57.9	1.19	0.33	0.07	13.78	15.96	0.12	1.77	0.45	0.10	0.02	0.01	0.02	0.45	<0.01	0.09	0.47	0.86
PNP05	colourless	1.1	2.8	4.1	61.7	1.91	0.27	0.24	6.39	19.62	0.16	0.72	0.70	n.d.	0.03	0.01	0.02	0.04	<0.01	0.07	0.003	0.33
PNP06	colourless	1.2	0.52	0.5	67.4	0.22	0.31	0.28	19.37	8.64	0.02	0.12	0.18	n.d.	<0.01	0.01	0.02	0.69	<0.04	<0.03	<0.16	2.26
PNP07	colourless	1.7	1.6	0.90	63.5	1.23	0.57	0.28	14.88	12.15	0.05	0.88	0.23	n.d.	0.01	0.05	0.05	0.49	0.06	<0.08	0.22	1.22
PNP12	colourless	2.0	2.8	5.3	59.0	1.73	<0.03	0.45	5.29	19.63	0.28	0.78	0.91	<0.01	0.02	0.01	0.03	0.03	<0.01	0.08	0.27	0.27
PNP16	colourless	1.1	3.2	4.9	59.2	1.96	0.19	0.18	6.72	19.88	0.28	0.89	1.01	<0.02	0.01	0.03	0.02	0.03	<0.01	0.1	0.37	0.34
	red layer	1.1	3.0	4.8	59.1	2.01	<0.04	0.15	6.76	18.91	0.28	0.90	0.94	<0.03	<0.02	0.91	<0.03	<0.01	<0.01	<0.03	0.32	0.36
PNP17	colourless	1.8	2.9	5.3	59.4	1.76	<0.02	0.41	5.37	19.86	0.26	0.81	0.87	<0.01	<0.01	<0.002	0.03	0.03	<0.01	0.09	0.24	0.27
CMOG B*	reference	17.00	1.03	4.36	62.27	0.82			1.00	8.56	0.09	0.25	0.34	0.05	0.01	2.66	0.19			0.02	0.12	
	measured	15.4	1.0	4.1	64.6	0.74			1.0	7.57	0.09	0.21	0.31	0.04	0.09	2.4	0.18			<0.02	0.06	
CMOG D*	reference	1.20	3.94	5.30	55.46	3.93			11.3	14.8	0.38	0.55	0.52	0.02		0.38	0.10			0.06	0.51	
	measured	1.4	3.7	4.9	57.5	3.9			10.2	12.9	0.35	0.42	0.45	<0.03		0.29	0.10			<0.03	0.27	

* Reference values taken from: BRILL, R. H. (1999). *Chemical Analysis of Early Glasses*. Corning, New York: The Corning Museum of Glass, p. 544.
n.d.: non-detected.

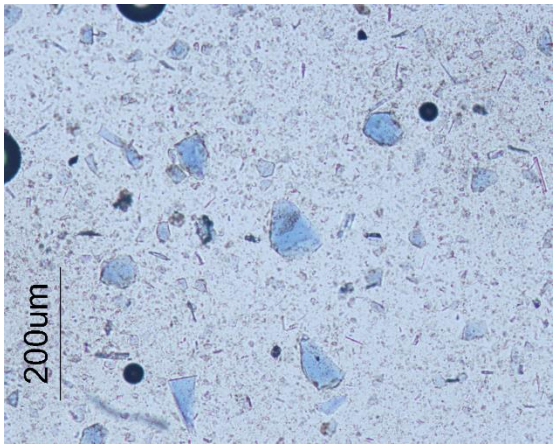
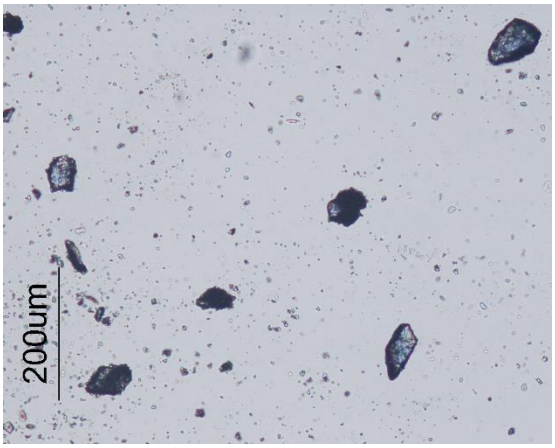
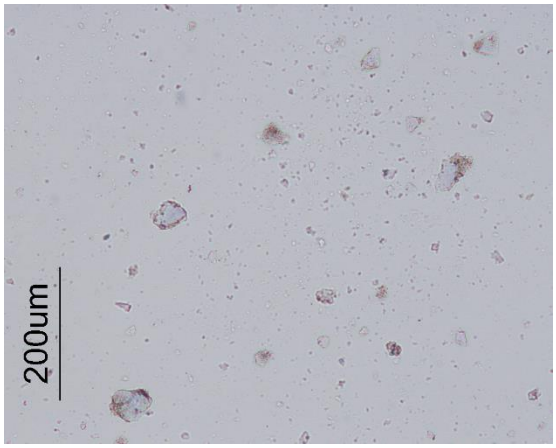
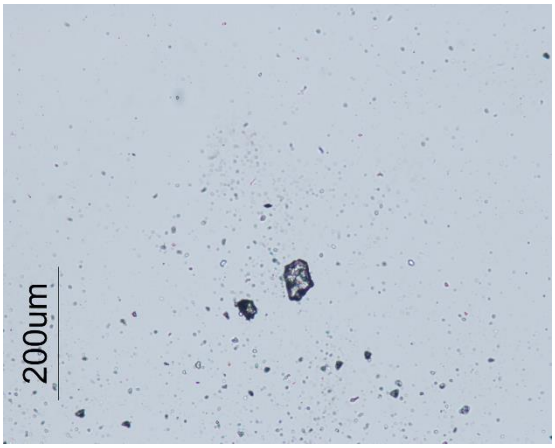
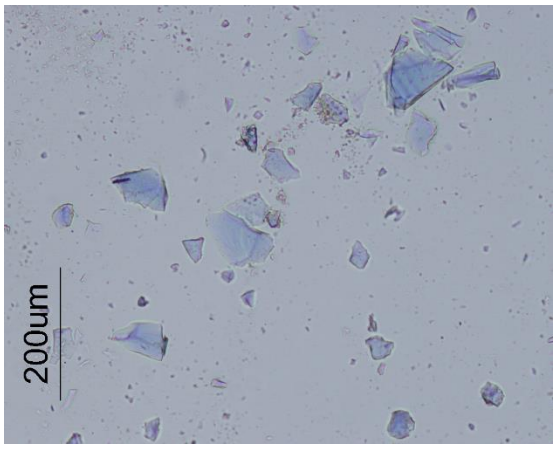
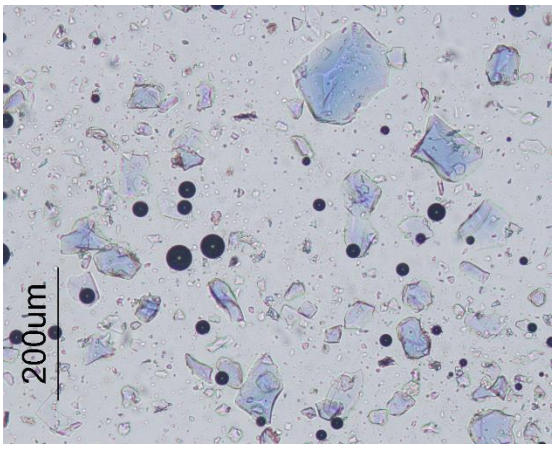
Table V.2 – μ- PIXE results for the paint layers from VCR and PNP sets (wt. %).

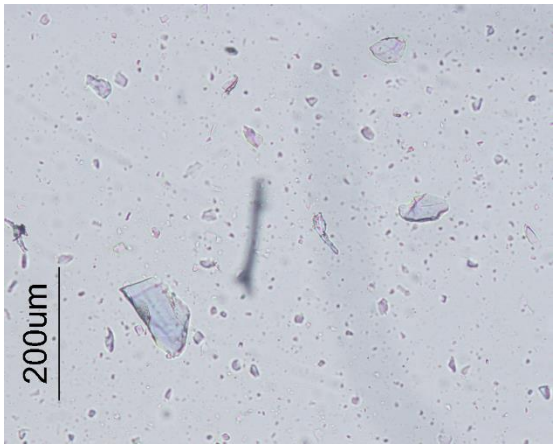
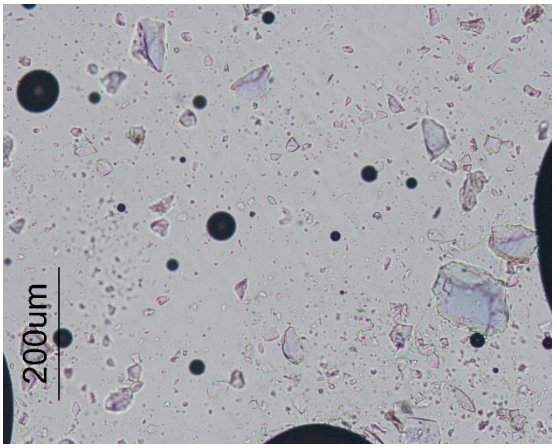
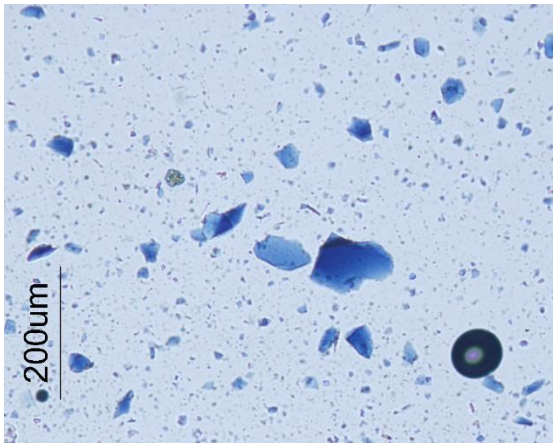
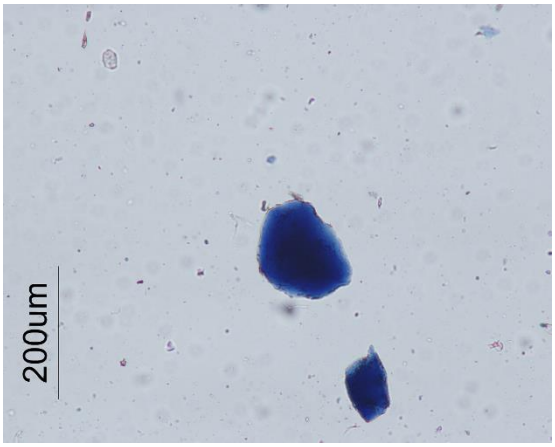
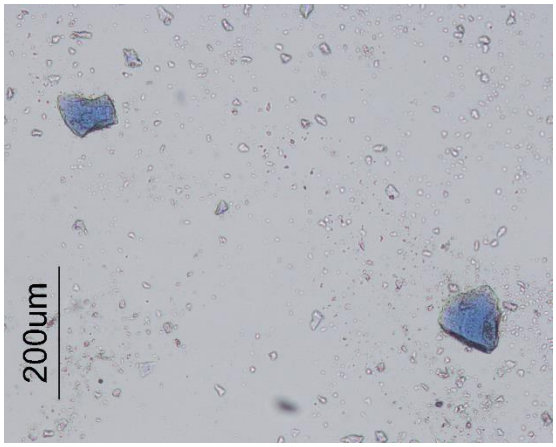
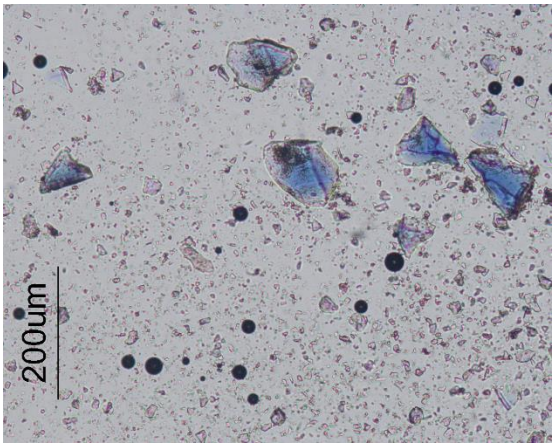
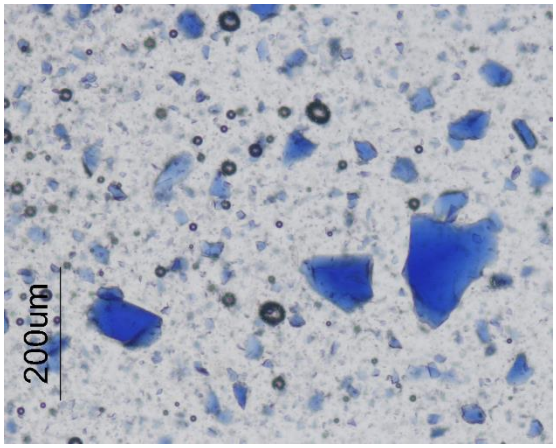
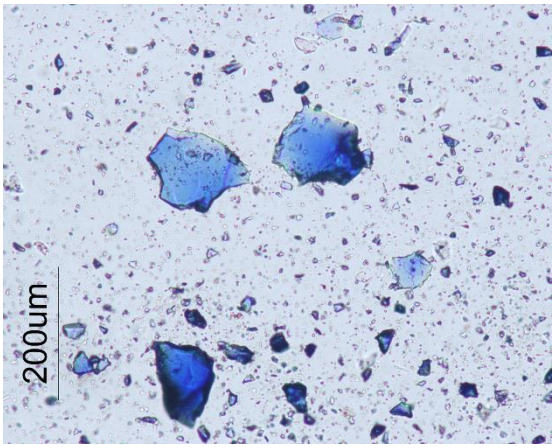
Sample	Colour	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_5	Rb_2O	SrO	BaO	PbO	Bi_2O_5	Ag_2O
VCR01	blue enamel	0.6	0.7	0.1	71.5	n.d.	n.d.	n.d.	14.79	0.41	0.03	<0.01	3.41	3.48	0.63	0.14	0.02	2.40	0.07	<0.01	<0.01	<0.34	1.16	n.d.
VCR02	blue enamel	5.9	0.3	0.9	68.3	n.d.	0.17	0.82	8.90	3.29	0.02	<0.02	1.67	2.14	0.16	0.08	0.04	1.66	<0.01	0.01	0.03	5.07	0.42	n.d.
VCR03	blue enamel	0.2	3.0	3.0	56.8	1.10	1.00	0.27	6.87	13.92	0.16	0.87	0.84	0.30	0.12	0.04	0.04	0.42	<0.03	<0.06	0.86	<0.16	<0.05	n.d.
VCR04	blue enamel	1.9	1.5	0.5	75.2	n.d.	n.d.	n.d.	12.06	0.49	0.05	0.06	2.32	2.21	0.50	0.11	0.04	3.16	<0.08	<0.03	<0.03	<0.76	1.05	n.d.
VCR05	blue enamel	6.2	0.2	1.0	69.6	n.d.	n.d.	0.78	8.41	2.50	0.03	0.04	1.59	2.18	0.18	0.08	0.03	1.66	<0.02	<0.02	0.03	5.13	0.45	n.d.
VCR05	grisaille	0.5	0.9	2.0	25.7	3.94	2.62	1.39	1.30	6.24	0.14	0.13	17.25	<0.31	n.d.	4.66	n.d.	n.d.	n.d.	n.d.	0.10	31.17	n.d.	n.d.
VCR06	sanguine red	8.5	0.7	2.5	68.0	0.31	0.10	0.19	2.22	14.99	0.14	0.13	0.54	n.d.	<0.01	1.79	0.01	0.02	<0.01	<0.01	0.04	n.d.	n.d.	n.d.
VCR12	grisaille	0.5	0.5	0.99	22.4	0.36	n.d.	0.59	0.58	5.02	0.32	0.05	6.40	n.d.	n.d.	18.55	n.d.	n.d.	n.d.	n.d.	<0.07	43.06	n.d.	n.d.
PNP05	grisaille	1.6	0.7	1.2	28.2	0.27	n.d	0.23	1.23	3.25	0.07	0.10	25.54	0.22	<0.03	9.41	0.17	n.d.	n.d.	n.d.	0.04	27.23	n.d.	n.d.
PNP12	blue enamel	2.4	<0.2	1.2	70.6	n.d.	<0.06	0.21	11.92	0.73	0.03	0.05	2.39	2.02	0.65	0.07	0.02	4.63	<0.09	<0.04	<0.07	<2.16	0.73	n.d.
PNP17	grisaille	1.1	1.5	3.1	41.2	n.d.	<0.33	0.59	3.10	10.30	0.17	0.32	11.23	n.d.	n.d.	3.09	n.d.	n.d.	n.d.	n.d.	0.57	19.35	n.d.	2.6
	blue enamel	2.1	<0.2	1.6	68.3	n.d.	<0.08	0.44	10.94	3.21	0.06	0.04	3.59	3.17	1.08	0.11	0.04	7.14	<0.1	<0.04	0.01	<3.04	1.35	n.d.
CMOG C*	reference	1.07	2.76	0.87	34.3	0.14			2.84	5.07	0.79		0.34	0.18		1.13	0.052			0.29	11.4	36.7		n.d.
	measured	1.2	2.4	0.9	36.4	<0.08			2.6	4.5	0.7		0.29	0.16		1.1	0.04			0.28	10.3	35.4		n.d.

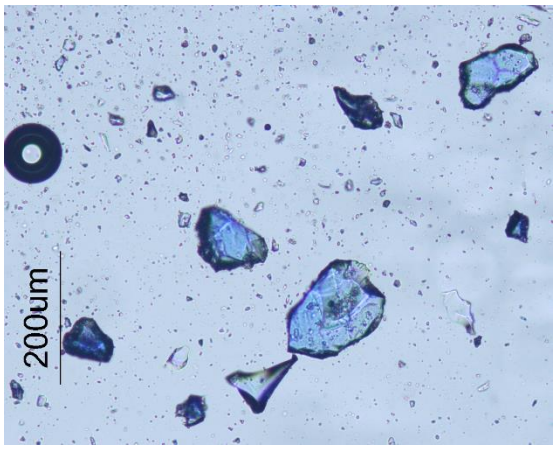
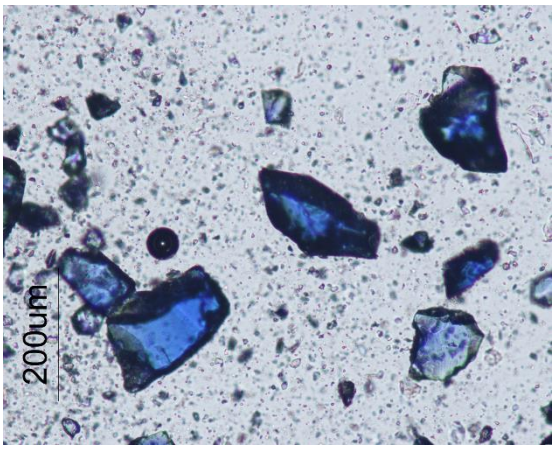
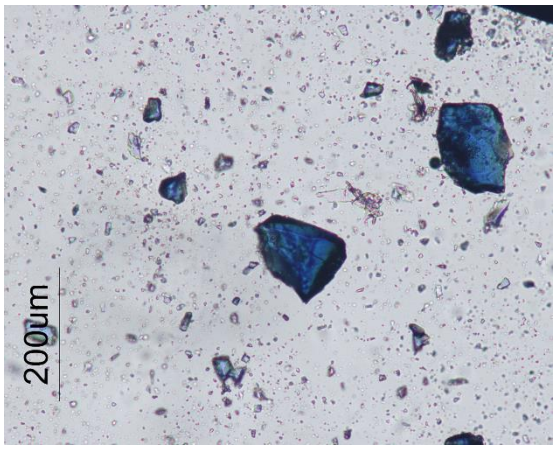
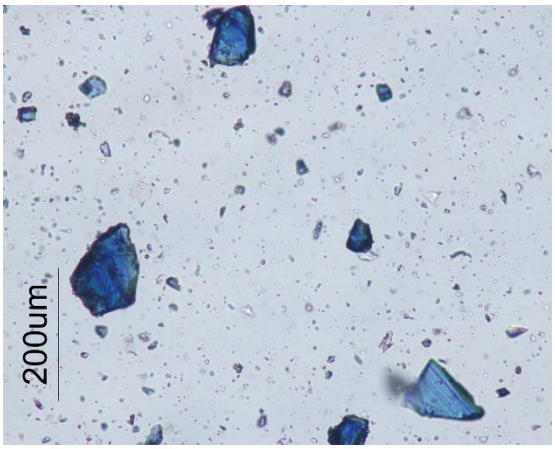
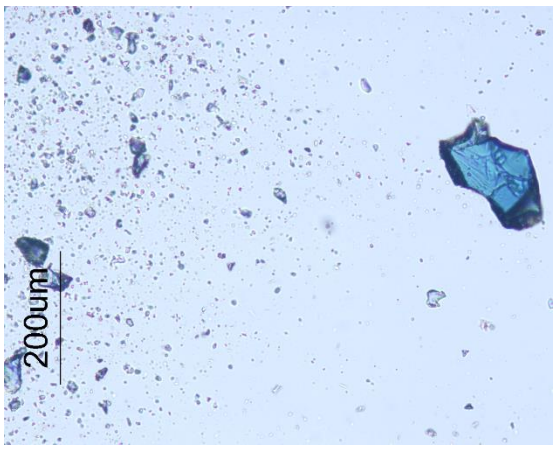
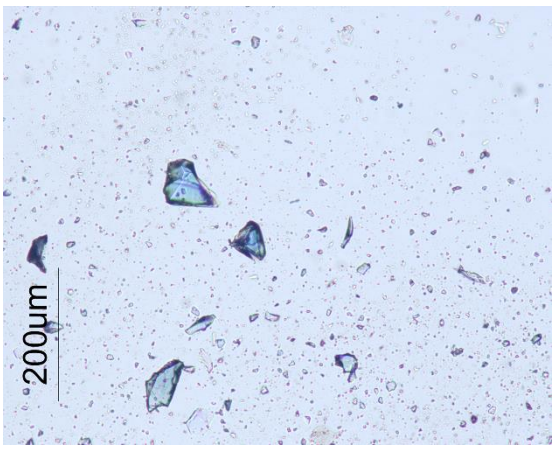
* Reference values taken from: BRILL, R. H. (1999). *Chemical Analysis of Early Glasses*. Corning, New York: The Corning Museum of Glass, p. 544.
n.d.: non-detected.

APPENDIX VI

OPTICAL MICROSCOPY OF BLUE ENAMEL POWDER SAMPLES SUBMITTED TO CORROSION

	Pristine	**Corroded**
R6B1Z		
R6B1S		
R6B2Z		

	Pristine	Corroded
R6B2S		
R8B1Z		
R8B1S		
R8B3Z		

	Pristine	Corroded
R8B3S		
R10B3Z		
R10B3S		

APPENDIX VII

UV-VIS SPECTRA OBTAINED FOR THE PRISTINE AND CORRODED ENAMEL POWDER SAMPLES OF BLUE ENAMEL RECIPES R6B2, R8B1, AND R8B3, WITH ZAFFER AND SMALT AS COLOURING AGENTS

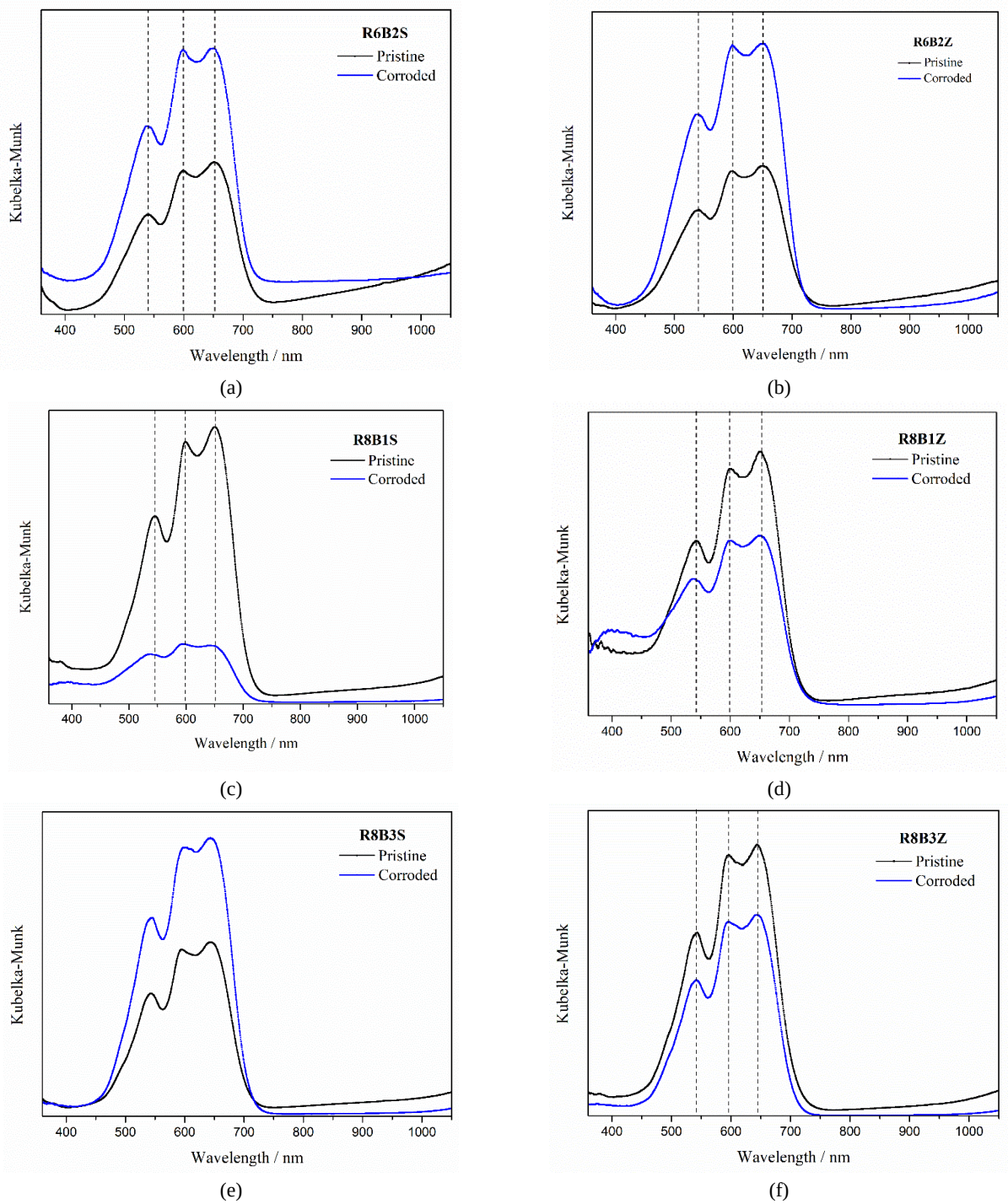


Figure VII.1 – UV-Vis absorbance spectra for enamel powder samples (a) R6B2S, (b) R6B2Z, (c) R8B1S, (d) R8B1Z, (e) R8B3S, and (f) R8B3Z, before and after corrosion.

APPENDIX VIII

FTIR SPECTRA OBTAINED FOR THE PRISTINE AND CORRODED ENAMEL POWDER SAMPLES OF BLUE ENAMEL RECIPES R6B2, R8B1, AND R8B3, WITH ZAFFER AND SMALT AS COLOURING AGENTS

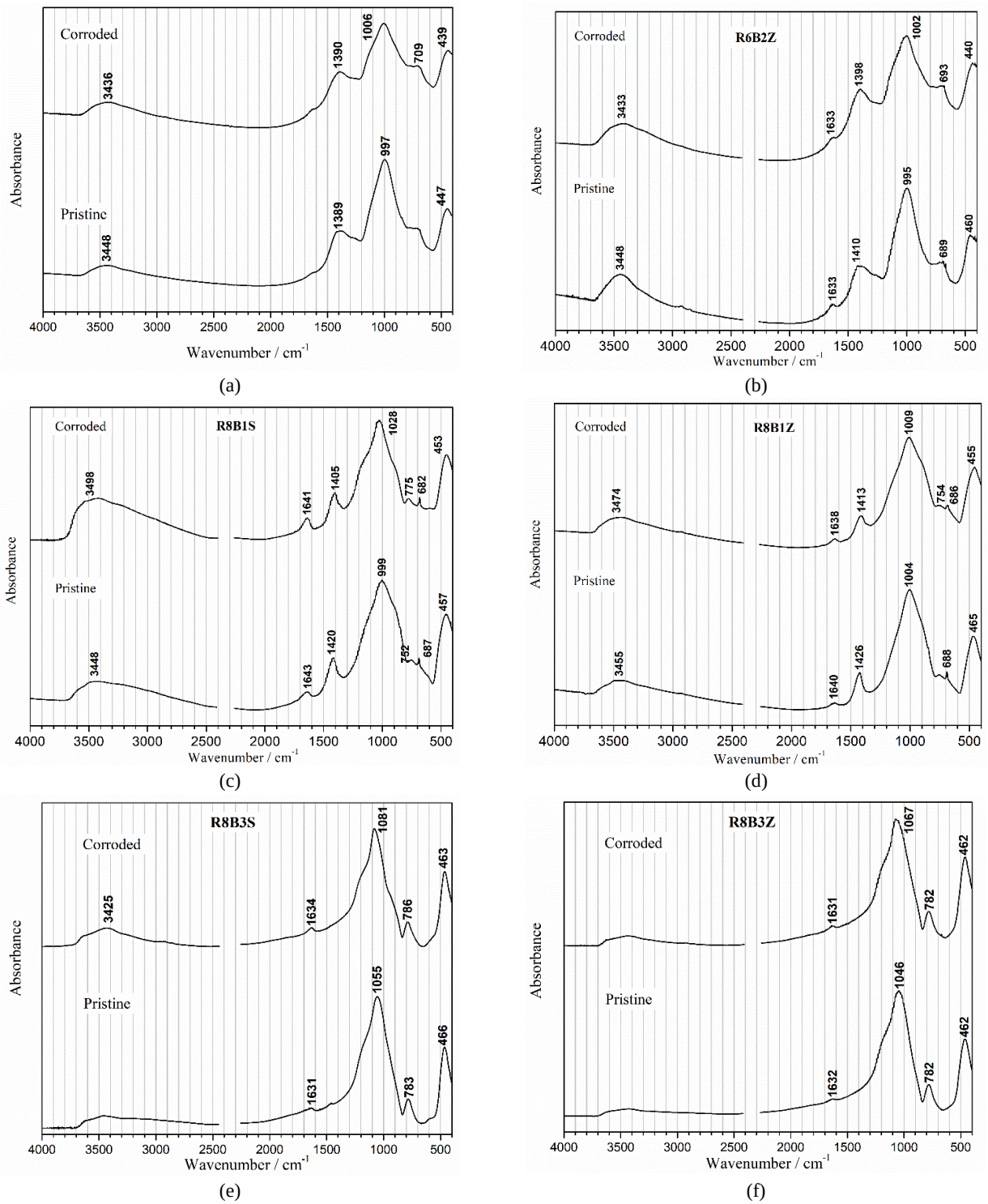


Figure VIII.1 – Infrared spectra for enamel powder samples (a) R8B1S, (b) R8B1Z, (c) R8B3S, and (d) R8B3Z, before and after corrosion.

APPENDIX IX

XRD DIFRACTOGRAMS OBTAINED FOR THE PRISTINE AND CORRODED ENAMEL POWDER SAMPLES OF BLUE ENAMEL RECIPES R6B2, R8B1, AND R8B3, WITH ZAFFER AND SMALT AS COLOURING AGENTS

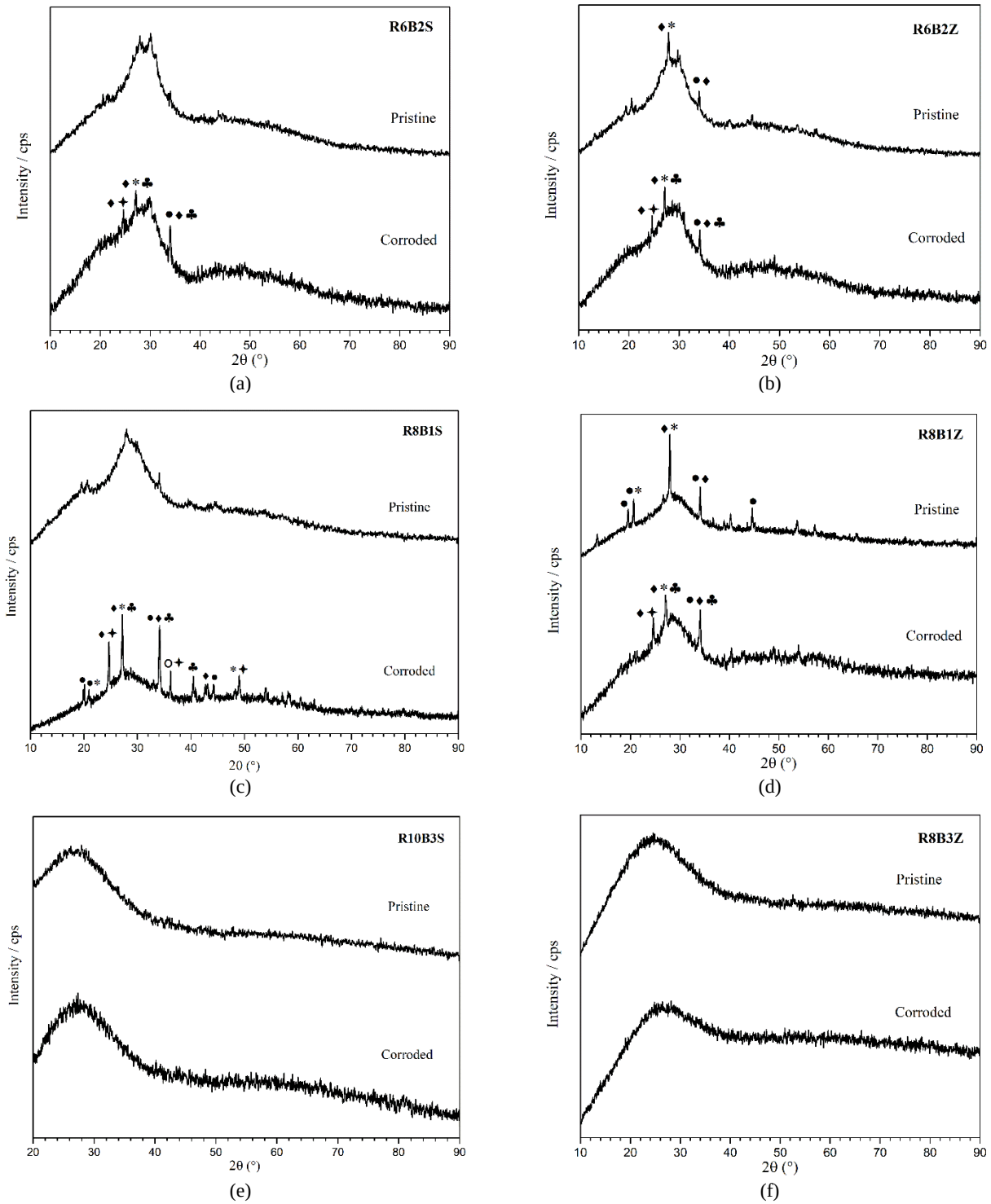
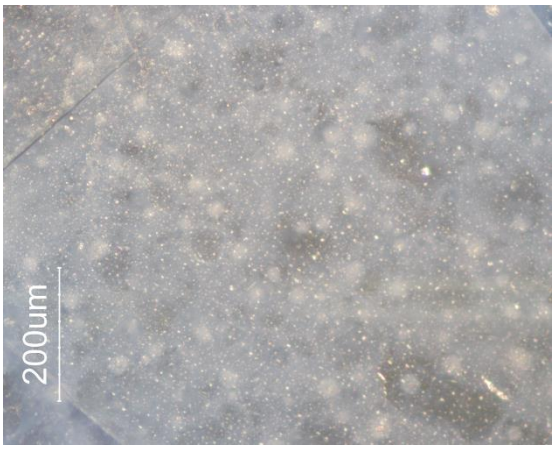
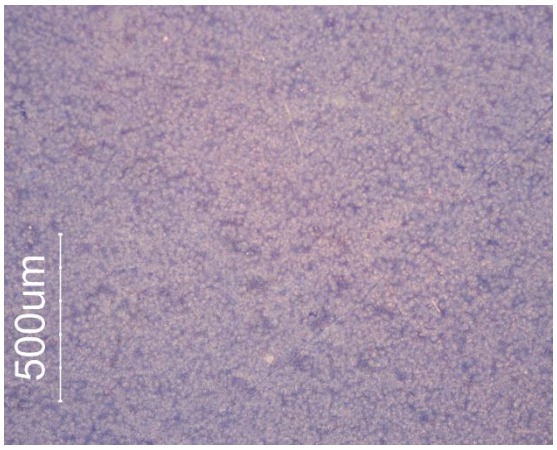
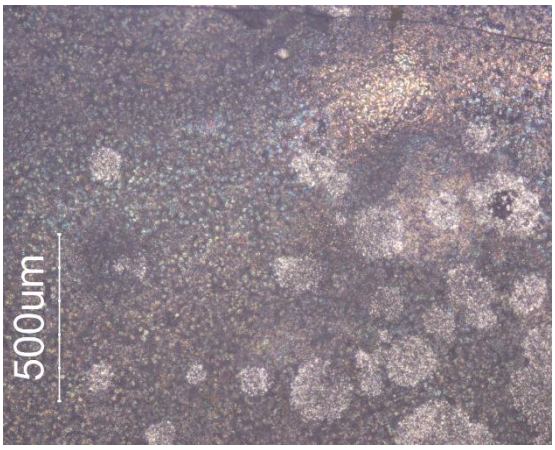
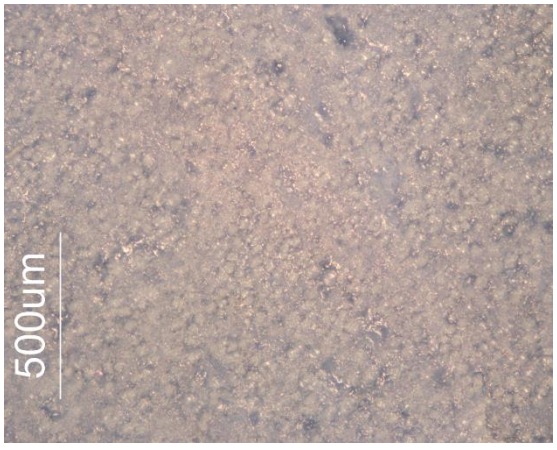
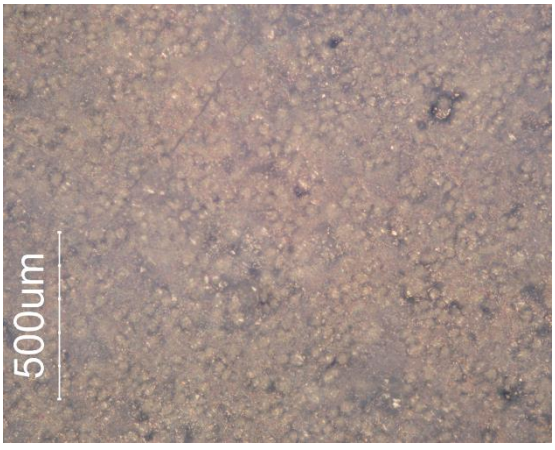
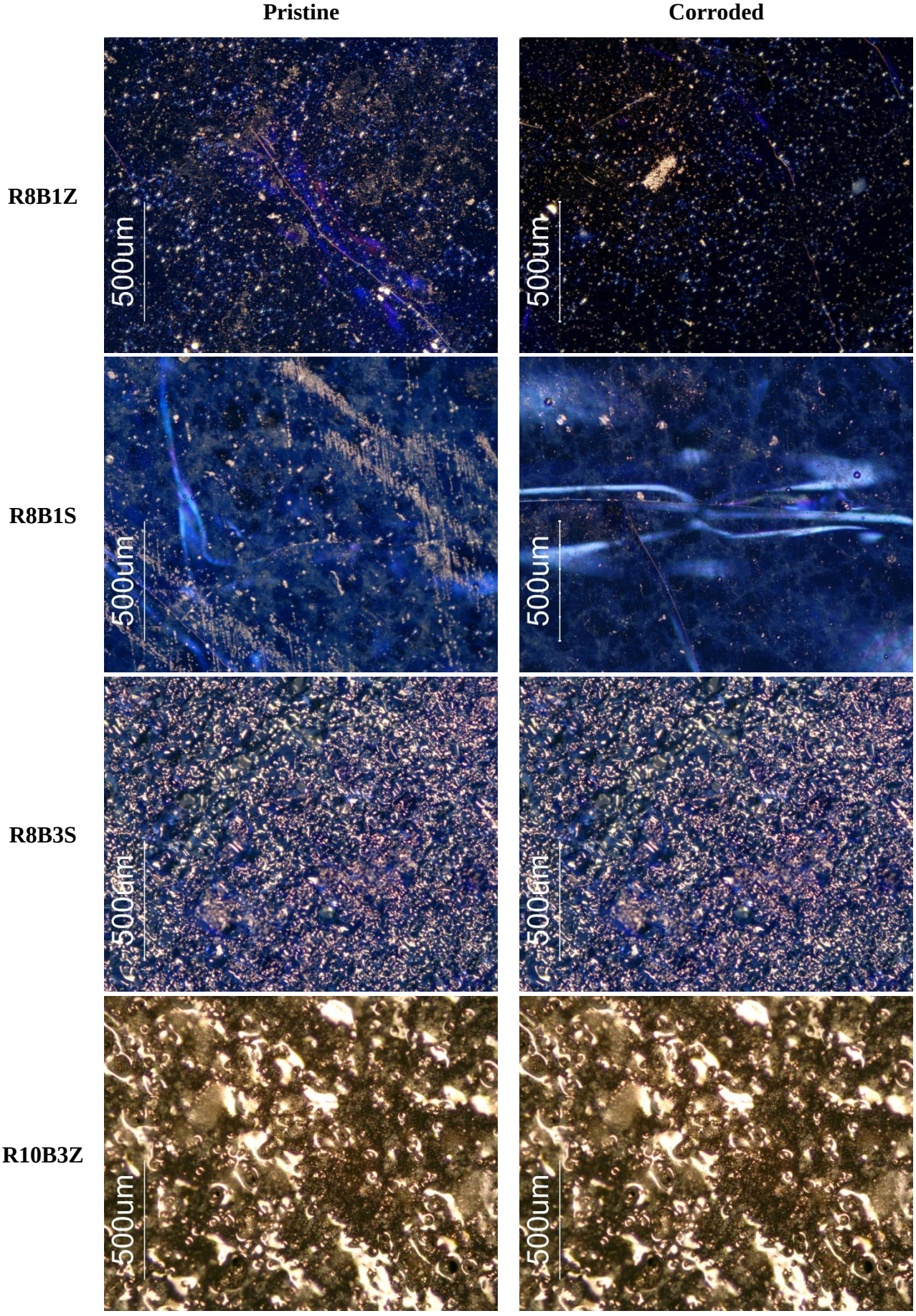


Figure IX.1 – XRD difractograms for enamel powder samples (a) R6B1S, (b) R6B1Z, (c) R8B1S, (d) R8B1Z, (e) R8B3S, and (f) R8B3Z, before and after corrosion.

APPENDIX X

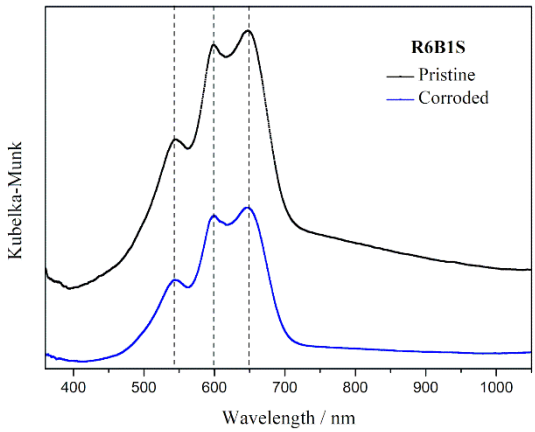
OPTICAL MICROSCOPY FOR ENAMEL PAINT SAMPLES, BEFORE AND AFTER CORROSION

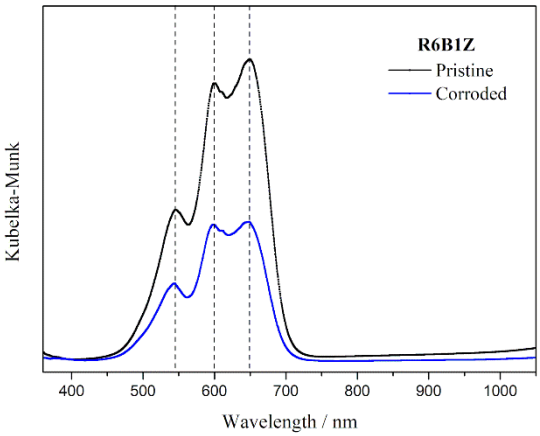
	Pristine	**Corroded**
R6B1S		
R6B2Z		
R6B2S		

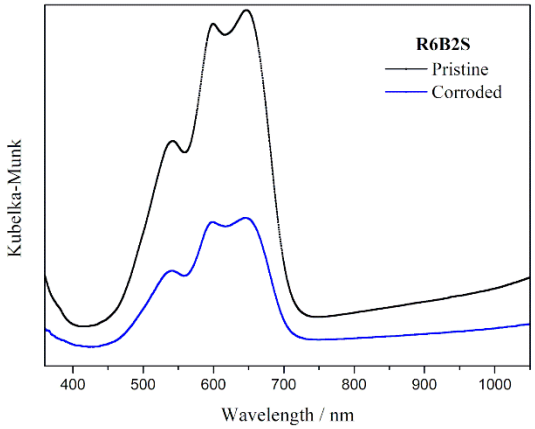

Pristine
Corroded
R8B1Z
R8B1S
R8B3S
R10B3Z
500um

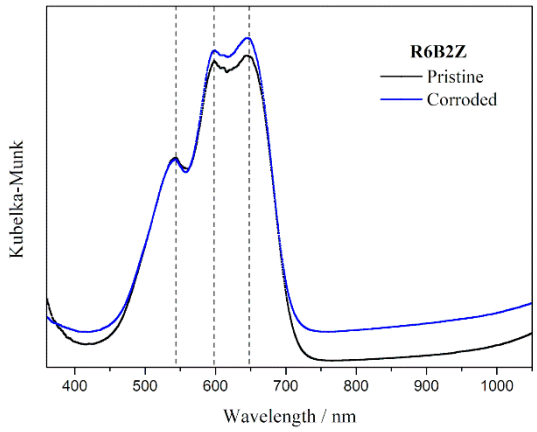
APPENDIX XI

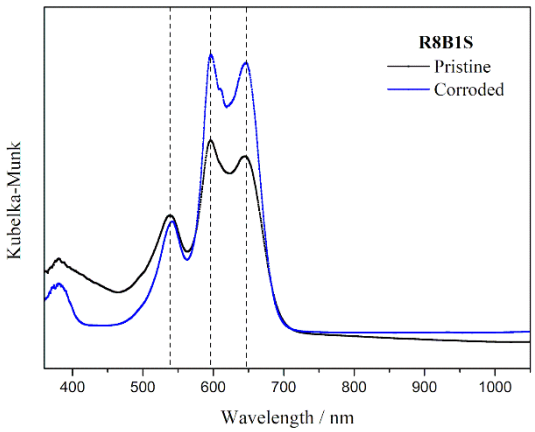
UV-VIS SPECTRA OBTAINED FOR THE PRISTINE AND CORRODED ENAMEL PAINT SAMPLES OF BLUE ENAMEL RECIPES R6B1, R6B2, R8B1, R8B3, USING ZAFFER AND SMALT AS COLOURING AGENTS, AND R10B3Z

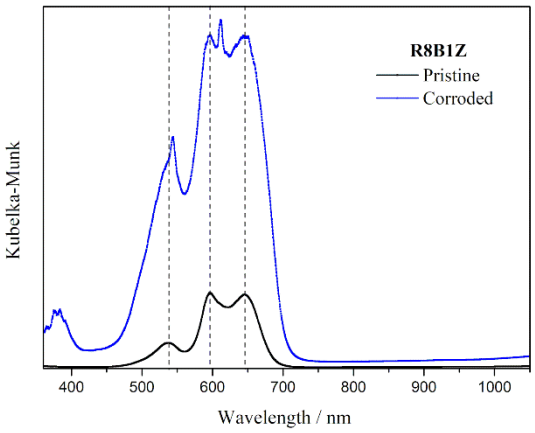


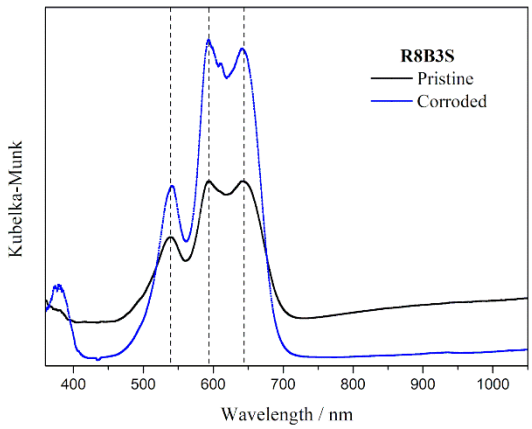


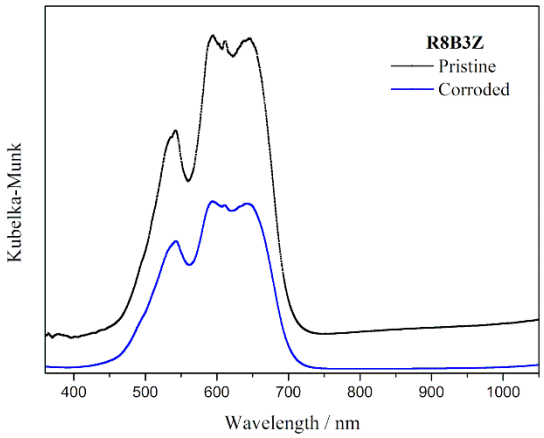


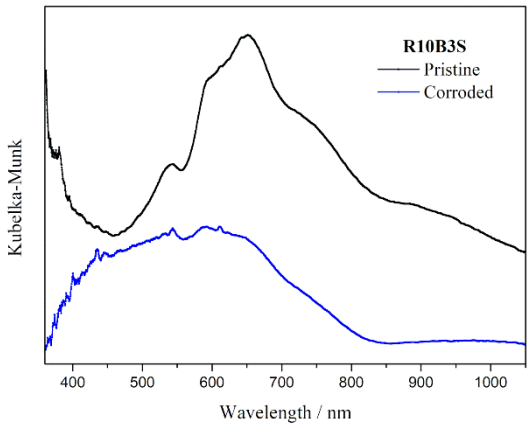







R8B3S
Pristine
Corroded
Kubelka-Munk
400
500
600
700
800
900
1000
Wavelength / nm


R8B3Z
Pristine
Corroded
Kubelka-Munk
400
500
600
700
800
900
1000
Wavelength / nm


R10B3S
Pristine
Corroded
Kubelka-Munk
400
500
600
700
800
900
1000
Wavelength / nm

APPENDIX XII

INFRARED AND RAMAN ASSIGNMENTS FOR POWDER AND PAINT SAMPLES OF SANGUINE RED PAINT

Table XII.1 - The IR assignments of the powder samples of sanguine red recipes R1, R2, and R4.

IR signature (cm^{-1})			**Assignment**	
R1	**R2**	**R4**		
710			δ CH_3COO^-	CH_3COO^- acetate
		726		$Pb_2Sb_2O_7$ (Bindheimite)
787	792		δ OH^-	α-FeOOH (goethite)
884	880-882			
937			ν CH_3COO^-	CH_3COO^- acetate
		953	Sb-O	Sb_2O_5 (antimony pentoxide)
	1019-1021		δ OH^-	γ-FeO(OH) lepidocrocite
1034			ν CH_3COO^-	CH_3COO^- acetate
	1162		δ OH^-	γ-FeO(OH) lepidocrocite
	1307-1318		ν NO^{3-}	NO^{3-} nitrate
1347			δ CH_3COO^-	CH_3COO^- acetate
1412			ν C–O	CH_3COO^- acetate
	1413-1425		ν NO^{3-}	NO^{3-} nitrate
1574			ν C–O	CH_3COO^- acetate
	1630-1635		δ H_2O	NO^{3-} nitrate
1709			ν CH_3COO^-	CH_3COO^- acetate
	3075		ν OH^-	γ-FeO(OH) lepidocrocite
	3116			
3205				
3401			ν OH^-	Molecular water
	3483		Surface OH^-	FeOOH

Table XII.2 – The Raman assignments of the painting sample R2.

Raman signature (cm^{-1})	Assignment
224	a_{1g} (sym. Str Fe-O)
243	e_g (sym. Bend Fe-O)
290	
407	
493	a_{1g} (sym. str Fe-O)
609	
655	asym str Fe-OH
1313	

Table XII.3 – The IR assignments of the powder samples of sanguine red recipe R3.

IR signature (cm^{-1})	Assignment	
667	δ Si-O	silicate
683		
690		
1038	Si-O-Si	
1065	C-O	Gum arabic
1215	asym. δ Si-O	Silicate
1396	δ C-H	Gum arabic
1600	ν C=O	
1994		
2116		
2910	ν C-H	Gum arabic
3321	ν O-H	

Table XII.4. – The Raman assignments of the painting samples R3, fired at 700 ºC.

Raman signature (cm^{-1})			Assignment
1 ºC / min	**2 ºC / min**	**5 ºC / min**	
225	224	221	a_{1g} sym. str Fe-O
245	244	238	e_g sym. bend Fe-O
292	291	286	
298	297		t_{2g} asym. bend Fe-O
411	409	402	e_g sym. bend Fe-O
497	496	491	a_{1g} (sym. str Fe-O)
611	610	603	
659	657	654	asym str Fe-OH
1318	1316	1302	

APPENDIX XIII

UV-VIS ABSORBANCE SPECTRA FOR POWDER AND PAINT SAMPLES R3, FIRED AT 700 ºC

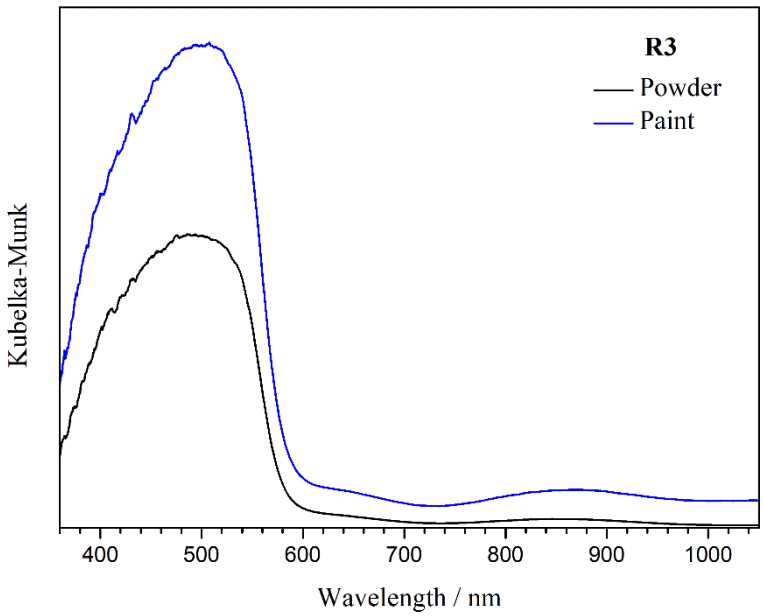


Figure XIII.1 – UV-Vis absorbance spectra of sanguine red recipe R3, for both powder and paint sample, fired at 700 ºC, with an annealing rate of 2 ºC /min.