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The fingerprinting of the materials used in Portuguese illuminated manuscripts: origin, production and specificities of the 16th century Antiphonary paints from the Biblioteca Pública de Évora

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A tese não inclui as criticas e sugestões do Júri

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ABSTRACT

This thesis focuses on the characterization of materials utilized within the illuminations of Codex 116c of Manizola, a large 16th century antiphonal housed in the Biblioteca Pública de Évora (BPE). Using various spectroscopic techniques (XRF, FTIR, Raman and SEM-EDS), a selection of illuminations were analyzed for pigment and binder identification. The manuscript was further analyzed using fiber optic reflectance spectroscopy (FORS), a non-invasive and portable analysis method ideal for use in illuminations. Using historical documentation and results gained from more extensive analysis of the manuscript, a collection of reference paint samples were created to be analyzed using this method. These samples serve as a reference not only to assist in the identification of pigments used within the manuscript, but also for future studies on similar materials allowing for a better understanding of manuscript production during the 16th century.

RESUMO

O presente trabalho é dedicado à caracterização dos materiais utilizados na produção das iluminuras do Codex 116c da Manziola do espólio da Biblioteca Pública de Évora (BPE). Trata-se de um antifonário de grandes dimensões produzido no séc XVI que deverá ter pertencido à Livraria de São Bento de Cástris. A identificação dos materiais utilizados na produção das iluminuras pode ser feita através de análises científicas. No entanto, alguns dos componentes das tintas utilizadas, especialmente os pigmentos orgânicos (lacas) e algumas misturas, apresentam obstáculos à sua identificação por métodos não invasivos. Através de várias técnicas espectroscópicas (XRF, FTIR, Raman e SEM-EDS), foi analisado um conjunto representativo de iluminuras, de modo a identificar os pigmentos e os ligantes presentes nas tintas. O manuscrito foi também analisado por FORS, um método portátil e não invasivo, ideal para a análise de iluminuras. Com base em documentos históricos e nos resultados analíticos, foi criado um conjunto de amostras de referência para ser analisado com FORS. Com esta abordagem, pretende-se que estas amostras, especialmente as de lacas, sirvam de referência não só na identificação dos pigmentos no manuscrito como em estudos sobre materiais semelhantes, contribuindo para um conhecimento mais aprofundado sobre a produção de manuscritos no séc XVI.

LIST OF ABBREVIATIONS

f.	Folio (manuscript page)
FORS	Fiber Optic Reflectance Spectroscopy
Log(1/R)	Apparent absorbance
MS	Manuscript
µ-FTIR	Micro-Fourier transform infrared spectroscopy
µ-Raman	Micro-Raman spectroscopy
r	Recto (of the folio)
SEM-EDS	Scanning electron microscopy and energy dispersive X-ray spectroscopy
UV-VIS-NIR	Ultraviolet-visible-near infrared
v	Verso (of the folio)
XRF	X-ray fluorescence spectroscopy
wt	Weight

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1. INTRODUCTION

1.1 A BRIEF HISTORY OF ILLUMINATED MANUSCRIPTS

Illuminated manuscripts are perhaps the most beautiful melding of art and word. These books, named for the application of gold used to decorate and highlight the illustrations or text within, are vibrant and engaging, creating an immediate sensory connection for the reader. This style of book originated in the third and fourth centuries with the development of the codex (Diringer, 1958; Watson, 2003). The vast majority of early manuscripts were created within monastic *scriptoria*, as these religious centers were also the main site of literacy and academic pursuits, until the development of the European book trade in the 13th century, which saw a proliferation of workshops outside of ecclesiastical settings (Watson, 2003). Even as the industry progressed past the use of parchment and books began to be printed, many types of books continued to made by hand, especially those with formats too complicated for the printing press of the time, such as large plain-chant choir books (Alexander J. J., 1992; De Hamel, 1986).

1.2 METHODS AND MATERIALS OF PRODUCTION

Until the 19th century and the development of the modern paint industry, artists were highly involved in the creation of the paints they were to use (Stulik, 2000). Far from the modern view of artists as working toward a personally inspired vision, throughout the medieval and Renaissance period works of art, including illuminated manuscripts, were created within a framework dictated by the patron and the ultimate function of the work. These specifications could include anything from subject-matter or iconography to the types of pigments used (Baxandall, 1988). Painters, scribes, and illuminators were thus considered craftsmen and while an apprenticeship system was likely the main source of instruction and artistic development, even within a monastic environment, hundreds of technical manuals were written within the medieval period alone detailing pigment, paint, and binder preparations and their methods of use (Alexander J. J., 1992; Clarke M. , 2011).

The development of the modern field of art history in the 19th century sparked an interest in these manuals and many important works have been translated, such as those compiled by Merrifield (1849), Cennino Cennini's *Il libro dell'arte* (Thompson Jr. D. V., 1933a), Theophilus' *On Divers Arts* (Hawthorne & Smith, 1979), and the medieval Judeo-Portuguese treatise *Libro de como si facem as cores* (Strolovich, 2005). Understanding the detailed processes by which artists worked is not always as clear or accurate as these books suggest. Many of these treatises were neither written by artists or craftsmen, nor were they necessarily written as practical instructions to be followed. They range greatly in their usability, often written with an assumed level of knowledge or complicate otherwise straightforward recipes with alchemical superstition, such as Theophilus' recipe for Spanish gold which calls for "basilisk powder" and the blood of a red-headed man (Hawthorne & Smith, 1979). That said, these books are an integral source of knowledge if one is to understand the processes of the artist, their original intent, and the artwork itself, especially if one intends to recreate these materials for more in-depth study.

By the 16th century, the book trade had grown to accommodate a more specialized production, and many pigments were available for purchase, minimizing the work necessary for their use (Thompson Jr. D. V., 1933a; De Hamel, 1986). This did not make it easy however: illuminators may not have had to create or refine the pigments themselves, but some processing was still necessary to achieve good quality paint. Grinding the pigment, using a flat stone muller against a hard slab of marble or porphyry, ensured that the pigment would be smooth and evenly dispersed (Thompson, 1936).

1.2.1 BINDERS

While pigments in the 16th century may have been sold already prepared, binders required constant preparation to keep them fresh and easily mixed with the pigment. Although oil-based binding media was widely used in easel painting throughout the Renaissance, polysaccharide and proteinaceous binders dominated manuscript illumination. One popular polysaccharide plant gum was arabic gum, a water-soluble gum sourced from the Acacia tree. While there are a number of varieties of Acacia, it is likely that the exact botanical source of the gum was unknown to artisans, and the gum of plum or cherry trees may also have been used. Plant gums were often mixed with small amounts of honey to create more strength and flexibility, as well as being a common binder for iron gall ink (Newman, 2000; Thompson, 1936).

Three main types of proteinaceous binders were used during this time period: parchment glue, glair, and egg yolk. Parchment glue, also called size, was created by heating small pieces of parchment in water to extract its collagen. This type of binding medium, and fish glue to a lesser extent, was primarily utilized as a ground for gilding (Thompson, 1936). While this material could be kept for long periods of time in its dried gelatin state, it must be melted again before each use (Newman, 2000).

Egg yolk, while very popular in panel painting, is too thick and soft to be used in manuscripts alone (Thompson, 1936). It can be a particularly enduring binding media, as the protein content (approximately 30%) denatures as it dries, resulting in a surface no longer soluble in water (Newman, 2000). In illuminated manuscripts egg yolk is primarily used in conjunction with other binders, usually glair, to create a slightly thicker and lustrous surface (Thompson, 1936).

Glair was arguably the most popular binder in manuscript illumination, frequently referenced throughout many of the treatises. This binding medium is created from egg white by beating the liquid to stiff peaks in order to break down a particular protein that gives egg white its viscous consistency. Once stiff foam is created, the mixture is left to rest and the glair (approximately 90% protein when dry), settles to the bottom ready to be mixed with pigment. Due to the lack of refrigeration, keeping glair fresh was a common concern. Some treatments included the addition of realgar, arsenic, vinegar, or cloves (Anonymous, 1596; Thompson Jr. D. V., 1933a; 1933b; Newman, 2000).

1.2.2 COMMON INORGANIC PIGMENTS

RED

Minium, also known as red or orange lead, is the pigment which originated the term “miniatures,” as it was the principal color (along with vermilion) used in manuscript texts (Diringer, 1958). Lead(II,IV) oxide (Pb_3O_4) is one of the oldest known synthetic pigments, made simply by grinding lead white and heating it until it turns red (Hawthorne & Smith, 1979). Cennini notes that it is not well-suited for use on walls or panel paintings, as it can darken considerably when exposed to air, though examples of this darkening have been found in manuscript painting, as well (Thompson Jr. D. V., 1933a; Fitzhugh E. W., 1986). While both the mineral and the artificial pigment are the same chemically and crystallographically, the synthetic version was highly preferred throughout its history (Fitzhugh E. W., 1986).

Vermilion (α-HgS) was similarly more popular than its natural mineral form of cinnabar. Likely invented by the Chinese and spread to Europe by the Arabs, early recipes for the preparation of vermilion are found in treatises from the 8th and 9th centuries, such as the *Mappae Clavicula* (Gettens, Feller, & Chase, 1993). One recipe found in *Libro de como si facem as cores* describes grinding quicksilver and sulfur together using a “dog’s foot with its hair and wool” and heating it (Strolovich, 2005). Experimental work by Miguel (2012) has showed that this strange suggestion actually allowed for easier incorporation of the materials and was not simply a superstition as had been previously assumed (Clarke M. , 2011). By the 15th century, however, this pigment was widely available and Cennini suggests simply purchasing it already prepared (Thompson Jr. D. V., 1933a). Exposure to light can cause the pigment to revert to black metacinnabar (α'-HgS), though darkening of the pigment within manuscripts is most often due to being mixed with other pigments that discolor such as minium or lead white (Thompson, 1936; Gettens, Feller, & Chase, 1993).

Red ochres, earth pigments containing hematite (Fe_2O_3), were plentiful and widely used within wall paintings, but were not often used in manuscript illumination due to their relatively dull coloring when compared to minium, vermilion, or red lake pigments (Thompson, 1936).

YELLOW

Yellow ochres, those containing limonite ($FeO(OH)\cdot nH_2O$) as well as a mixture of quartz and clays, come in a variety of colors ranging from pale yellow to brown and can be heated to create darker ‘burnt’ ochres (Eastaugh, Walsh, Chaplin, & Siddall, 2004; Clarke M.

, 2011). This type of earthen pigment was similarly not highly favored in book painting. Any instance that the illuminator wanted to brighten or color an area with yellow, gilding or the following yellow pigments would give a much better result (Thompson, 1936).

Lead-tin yellow is the name for two varieties of yellow lead tin oxides used throughout the 14-18th centuries. Type I is made up of Pb_2SnO_4. Type II, made by heating Type I with silica, can be described as $Pb(Sn_{1-x}Si_x)O_3$, where x ~¼ (Eastaugh, Walsh, Chaplin, & Siddall, 2004). This opaque and lightfast pigment was often recommended to be mixed with a variety of blue pigments to create a green. Like many pigments, this type was referred to by many names, often *giallorino* or, confusingly, *massicot,* which later referred to a different pigment composed of lead(II) oxide (Kühn, 1993).

Orpiment (As_2S_3), named *auripigmentum* by Pliny due to its brilliant color, is a mineral often found in association with realgar (red arsenic sulfide, AsS or As_4S_4). This pigment was originally imported to Europe through Asia Minor, however by the 14th century it could be artificially prepared by sublimating arsenic and sulfur. It is extremely toxic and is known to fade when exposed to the air. Realgar is even less stable and is known to oxidize to orpiment or pararealgar (Fitzhugh E. W., 1997). While it was often suggested to mix with indigo to create green, it was not recommended to be used with copper or lead-based pigments, as it causes them to darken even when simply painted nearby (Thompson, 1936).

GREEN

Malachite, basic carbonate of copper ($CuCO_3.Cu(OH)_2$), is a mineral that is often found in association with azurite. It is often fairly coarse in texture, as excessive grinding causes the color to fade. While not frequently referred to in treatises, this pigment has been found frequently in manuscripts and easel paintings throughout the medieval and Renaissance period (Gettens & Fitzhugh, 1993; Thompson, 1936).

Verdigris is the name applied to a variety of copper acetates. This synthetic pigment has been prepared using a number of techniques, primarily by placing a copper plate in a vase with vinegar, sealing it with dung, and burying it for some number of days while the metal inside corrodes (Merrifield, 1849). Variations within the recipe, as well as the composition of the ingredients, generally results in one of the following: $[Cu(CH_3COO)_2]_2 \cdot Cu(OH)_2 \cdot 5H_2O$; $Cu(CH_3COO)_2 \cdot Cu(OH)_2.5H_2O$; $Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_2$; or $Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$, only the last of which appears green rather than blue. The resulting corrosion can be scraped off and used immediately, or ground with acetic acid to create neutral copper acetate, $Cu(CH_3COO)_2 \cdot H_20$ (Kühn, 1993). Historical documents, such as Cennini, warn of the inevitable fading of this bright pigment to a dull brown (Thompson Jr. D. V., 1933a).

BLUE

Of the inorganic blues used throughout the medieval and renaissance period, two minerals stand out clearly: azurite and lazurite. Lazurite, sourced from *lapis lazuli*, was highly prized for its brilliant blue hue. It is a mineralized limestone, with a complex structure: $(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$. Also known as ultramarine (though this term is often used today to refer to the synthetic form developed in the 19th century), this pigment was exceptionally expensive, sourced primarily from the Kokcha River valley of Afghanistan, and required complex methods of preparation (Plesters, 1993; Eastaugh, Walsh, Chaplin, & Siddall, 2004). Unlike other mineral pigments that can be simply washed and ground, the same treatment of lazurite would result in a dull, grey color. An extraction method was developed in at least the 14th century, as evidenced by many of the treatises: the powder must be mixed and pounded with a variety of gums and waxes before washing the resulting malleable solid in lye, which draws out the characteristic, bright blue pigment (Thompson Jr. D. V., 1933a; 1936; Plesters, 1993). This process took a number of days to complete and the resulting pigment cost as much as gold. By the 17th century, Portuguese writer Nunes noted that the cost had become too much and, while lessening in usage overall, would most likely be painted over a ground of azurite as a cost-saving measure (Eastaugh, Walsh, Chaplin, & Siddall, 2004).

Azurite has been used since antiquity and offered a more accessible and affordable option for rich, opaque blues. This pigment is made up of basic carbonate of copper ($2CuCO_3 \cdot Cu(OH)_2$) and was much easier to prepare than lazurite. By simply grinding and washing to separate out impurities, a light or dark blue could be created depending on how finely it was ground (Gettens & Fitzhugh, Azurite and Blue Verditer, 1993). In contrast to lazurite, azurite could be sourced throughout Europe, especially in France, Spain, and Germany (Thompson, 1936).

Synthetic forms of copper-based blue pigments are also frequently mentioned within the treatises, produced via a number of methods. Some were created from combinations of calcium carbonate and copper sulfate; others from copper, lime, and ammonia; and many more recipes calling for the corrosion of silver using some form of vinegar or ammonia. The use of silver is puzzling as, even if there were some copper impurities, the process would not produce a blue compound. The other two methods can create successful alternatives. However, while they may have been a cheaper alternative, these synthetic blues were often difficult to make consistently and could suffer from color change (especially in the case of those containing cuprammonium salts) (Thompson, 1936; Eastaugh, Walsh, Chaplin, & Siddall, 2004; Gettens & Fitzhugh, Azurite and Blue Verditer, 1993).

Another blue pigment used during this time period is smalt, a potassium cobalt glass [cobalt(II) silicate, $CoO\ nSiO_2$ ($+ K_2O + Al_2O_3$)]. Likely developed in the Near East, this pigment gained popularity in European easel painting throughout the 16th-17th centuries, especially as a siccative to be used in combination with other blue pigments that dry slowly in oil, before being supplanted by Prussian blue and synthetic ultramarine (Mühlthaler & Thissen, 1993). It was used in manuscript illumination during the Renaissance, often in mixture with azurite (Clarke M. , 2001a; Scott, et al., 2001; Čechák, Trojek, Musílek, & Paulusová, 2010). Similar to azurite, the color of smalt can vary in intensity depending on how finely it is ground. Unfortunately, due to the instability of the potassium-based glass, it has a tendency to turn grey over time and in poor environmental conditions (Eastaugh, Walsh, Chaplin, & Siddall, 2004; Mühlthaler & Thissen, 1993).

WHITE

Lead white was by far the predominately used white pigment from antiquity to the 19th century. Also referred to as *ceruse*, this pigment is made up of basic lead carbonate ($2PbCO_3{\cdot}Pb(OH)_2$). Like many other pigments, it occurs naturally in the form of cerussite, which was very rarely used. (Eastaugh, Walsh, Chaplin, & Siddall, 2004) It was prepared much in the same way as verdigris: by sealing lead plates in a container with vinegar or urine and grinding the resulting corrosion product (Hawthorne & Smith, 1979). It is lightfast, but can darken when exposed to sulfur either in the air or due to nearby sulfur-based pigments, such as orpiment (Gettens, Kühn, & Chase, 1993).

Other white pigments, such as gypsum ($CaSO_4{\cdot}2H_2O$) or calcium carbonate ($CaCO_3$, sourced from chalk, limestone, marble, or mollusk shells) were occasionally used as pigments, but were far more often utilized as grounds and extenders (Gettens, Fitzhugh, & Feller, 1993).

1.2.3 COMMON ORGANIC PIGMENTS

Organic or lake pigments are those that have been sourced from organic dyes in order to create an insoluble compound that may be used for painting. Dyestuffs, the water-soluble material from which dyes are extracted, have been used for millennia to color textiles (de Graaff, Roelofs, & van Bommel, 2004). It is important to understand the fundamental techniques associated with dyeing as lake pigments, in particular those made from insects, have historically been created by extracting the dye from a textile rather than from the dyestuff itself (Thompson, 1936).

DIRECT DYES

Direct dyes are the simplest forms of dyes and can suffer from loss of color from the textile due to light or washing. This is because this type of dye is only bound to the surface of a material via van der Waals forces, dipole interaction, and hydrogen bonding (de Graaff, Roelofs, & van Bommel, 2004). Direct dyes contain water-soluble molecules, such as crocetin in saffron or curcumin in turmeric, which require no treatment of either the dye nor the fiber, but may also be treated as mordant dyes to improve their fastness (Kirby, van Bommel, & Verhecken, 2014).

VAT DYES

Vat dyes are indigoid dyes, such as those found in indigo or woad and the brominated form found in some types of shellfish. These naturally insoluble dyes require a specific treatment in order to dye fibers or material (Cardon, 2007). This multi-step process involves the reduction of the dye to a water soluble *leuco*- form, which can be absorbed into the fibers submerged in the vat. Upon removal from the vat, the dye oxidizes to its insoluble form and is fully attached to the fibers (Kirby, van Bommel, & Verhecken, 2014).

MORDANT DYES

Mordant dyes are the largest group of dyes and the type most commonly associated with the production of lake pigments. These use a mordant, a water soluble metal salt, that attaches to the fabric. Upon adding this prepared textile to a dye bath, a dye-metal-textile complex is created, attaching the dye to the coordination metal via neighboring C=O and C-OH groups (Kirby, van Bommel, & Verhecken, 2014). The most common mordant used throughout the Medieval and Renaissance period was alum, though mordants containing iron, copper, and tin were also used, each of which affects the ultimate color of the dyed textile (Cardon, 2007; de Graaff, Roelofs, & van Bommel, 2004).

LAKE PIGMENT MANUFACTURE

Lake pigments could be made by extracting the dye directly from the dyestuff or through dyed textiles, called shearings, and preferred methods for doing so varied by time period. Up until the 19th century, dyes were typically extracted using an alkaline solution, often lye (potassium carbonate) (Kirby, van Bommel, & Verhecken, 2014). This extracted dye was then precipitated onto a substrate. During the 12th-18th centuries, the most common substrate was potash alum, or potassium aluminum sulfate ($AlK(SO_4)_2 \cdot 12H_2O$) (Kirby, Spring, & Higgitt, 2005). This material was mined and, in high demand for use primarily in the textile industry, was of great economic importance throughout the Medieval and Renaissance periods. The primary source of alum from the mid-15th-18th centuries were the Tolfa mines north of Rome (Delamare & Guineau, 2000).

Once washed and dried, the resulting pigment required very little grinding and was tempered with a binder to create a transparent paint that was often used for glazing. For more opaque pigments, extenders such as calcium carbonate or gypsum could be added either within the production of the lake pigment or mixed together afterward (Kirby, van Bommel, & Verhecken, 2014).

Numerous varieties of lake pigments were used in illuminated manuscripts. The following is not a comprehensive list of such pigments, but rather a summary of those most commonly used.

RED LAKES

BRAZILWOOD

Figure 1: Left, brazilin. Right, brazilein.

Brazilwood dye comes from the *Caesalpinia* trees after which the country of Brazil is named. Prior to the discovery of region in the 16th century, similar dyes sourced from sappanwood were imported from Southeast Asia. (Eastaugh, Walsh, Chaplin, & Siddall, 2004) The main chromophore found in this material is brazilin, a homo-isoflavonoid, which readily oxidizes to form brazilein (Figure 1) (Cardon, 2007). Like many dyes including the anthraquinones discussed below, brazilwood is pH-sensitive becoming more red in acidic solutions (Clarke M. , 1999). This quality was well known to artists and is reflected in the recipes, such as that in the 17th century Paduan MS:

> “80. To make brazil wood of four colours. – Take brazil wood, and steep any quantity you please (so that it is more than a third part) in clear water until the colour is very red. Then divide this colour into 4 parts: if you wish to make a rose colour use it pure; if you wish it purple add lime water, but the water must be tepid; if you wish a violet colour add a ley to it; and if you desire that it should be of a mulberry colour add tartar” (Merrifield, 1849).

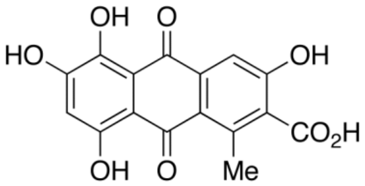
MADDER

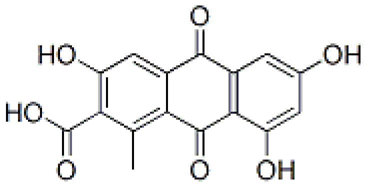
Figure 2: Left, alizarin. Right, purpurin.

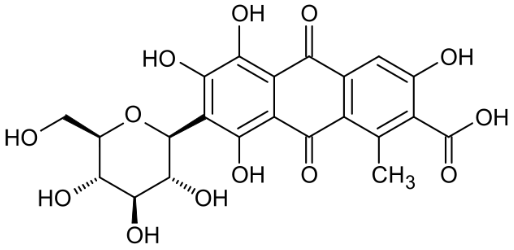
Madder lakes are made from the roots of the perennial plants of the *Rubia* genus. In Europe, the predominately cultivated species used was *Rubia tinctorum*, which was brought from Asia by the Moors, with locally grown wild madder (*Rubia peregrina)* being used earlier (Schweppe & Winter, Madder and Alizarin, 1997). The primary chromophores associated with madder are alizarin and purpurin, both anthraquinones, and as stated above they can range from red to purple depending the pH used during the lake preparation (Figure 2) (Eastaugh, Walsh, Chaplin, & Siddall, 2004). Unlike brazilwood, which was extracted directly from the plant matter, madder lakes were primarily sourced from dyed textiles by dissolving the wool fibers in strong alkaline solutions, creating a partially proteinaceous substrate. (Kirby, van Bommel, & Verhecken, 2014)

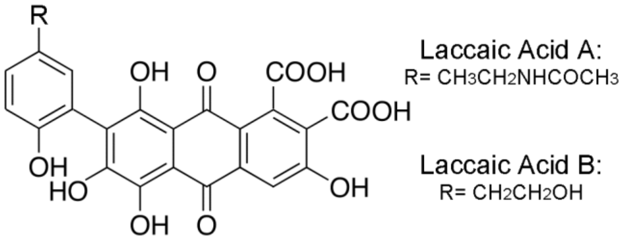
Table 1: Percentage of chromophores found in common insect dyestuffs (de Graaff, Roelofs, & van Bommel, 2004)

	Kermesic Acid	**Flavokermesic Acid**	**Carminic Acid**	**Laccaic Acid**
Kermes *Kermes vermilio*	75-100%	0-25%	-	-
Polish Cochineal *Porphyrophora polonica*	13-38%		62-88%	-
Armenian Cochineal *Porphyrophora hameli*	1-4.2%		95-99%	-
Mexican Cochineal *Dactylopius coccus*	0.4-2.2%		94-98%	-
Lac *Kerria lacca*	3.6-9.0%		-	A: 71-96% B: 0-20%


Kermesic Acid


Flavokermesic Acid


Carminic Acid



Laccaic Acid

The commonly utilized insect dyestuffs are sourced from the egg laying females of the superfamily Coccoidea, commonly referred to as scale insects. This includes lac insects (*Kerria lacca),* kermes (*Kermes vermilio),* Polish cochineal (*Porphyrophora polonica*), Armenian cochineal (*Porphyrophora hameli*), and Mexican cochineal (*Dactylopius coccus*) (de Graaff, Roelofs, & van Bommel, 2004).

Lac insects, from which the term lake pigment is derived, are indigenous to Southeast Asia. In addition to being a source of red dye, the protective gum they create is the basis of shellac. This dye, made up of both kermesic and laccaic acids, was extracted from the gum directly or from dyed textiles (Table 1) (Eastaugh, Walsh, Chaplin, & Siddall, 2004).

The rest of the scale insects are similar to one another. Until the discovery of the Americas, kermes was favored over other scale insects, having a larger percentage of dyestuff and more efficient harvesting methods (Polish and Armenian cochineal both live on the roots of plants, requiring the removal of the entire plant) (Schweppe & Roosen-Runge, 1986). New World cochineal was found to be highly concentrated with dye and the indigenous populations were actively cultivating them. A formal order was made in 1523 by the Spanish court to begin collecting as much cochineal as possible, resulting in regular shipments to Spain. By the 1580s, these shipments included many tons of the dyestuff, which was sold and distributed widely influencing artworks and sumptuary laws across Europe (Phipps, 2010).

YELLOW LAKES

WELD

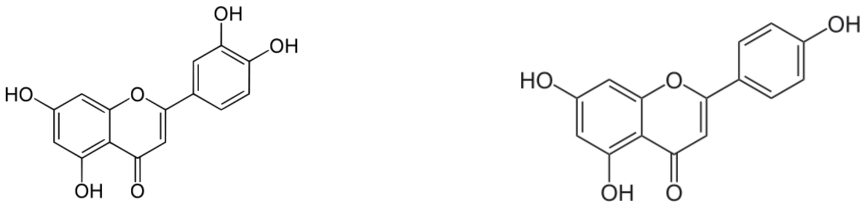


Figure 3: Left, Luteolin. Right, Apigenin.

Reseda luteola, known as weld or dyer’s rocket, was a widely used throughout Europe until the late 18th century and the discovery of quercitron from North America (de Graaff, Roelofs, & van Bommel, 2004). This bright yellow lake gets its color primarily from flavonones such as luteolin and apigenin and was commonly extracted directly from the plant (Figure 3).

BUCKTHORN

Figure 4: Left, Rhamnetin. Right, Quercetin.

The fruit of the buckthorn tree, also called Avingon or Persian berries, primarily contains flavonols rhamnetin and quercetin (Figure 4) (Cardon, 2007). Unripe berries are used to create a warm, yellow lake, which was sometimes called *dutch pinke*, while ripe berries yield a green pigment. These lakes are similarly created directly from the plant matter (Kirby, van Bommel, & Verhecken, 2014).

GREEN LAKES

In addition to sap green, the green buckthorn lake described above, iris green was also written of frequently in the treatises. This lake was prepared in a different manner than usual, often simply mixing the juice with alum and quicklime (Merrifield, 1849). Similar green pigments were created from a variety of other sources such as rue, parsley, and asparagus seeds, however the majority of the color likely comes from chlorophyll, making it very likely to fade. Overall, creating green from mixtures was a far more popular and recommended method (Eastaugh, Walsh, Chaplin, & Siddall, 2004).

BLUE AND VIOLET LAKES

INDIGO

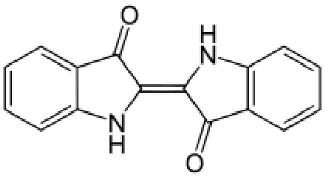


Figure 5: Indigotin

Indigo dye can be sourced from a variety of plants, the most common being true indigo, *Indigofera tinctoria,* and woad, *Isatis tinctoria*. As briefly discussed earlier, indigo is a vat dye and, once extracted from the plant itself, it is insoluble and ready to be mixed as a pigment with no further treatment. (Figure 5) The extraction itself takes the form of a multi-day fermentation using an alkaline solution and heat. The plant matter is then oxidized through vigorous mixing, resulting in a precipitate that is dried and ready for use (Eastaugh, Walsh, Chaplin, & Siddall, 2004). While woad was readily available in Europe, indigo was imported from the East and highly prized. In addition to being a pigment source, the rest of the woad plant was utilized as a high quality source of potash, due to the plant’s ability to absorb excess salts from the soil (Thompson, 1936).

TURNSOLE

Known by a number of names: turnsole, folium, torna-ad-solem, and others, this dye is sourced from the plant *Chrozophora tinctoria* (Eastaugh, Walsh, Chaplin, & Siddall, 2004). While this dye, like many of those previously discussed, can range in color, it was most frequently used in its purple form. When used as a paint, it was not prepared as a lake, but rather soaked into pieces of cloth that had been previously treated to bring out the desired color (plain cloth for red, lime water for purple, and lime water followed by exposure to ammonia vapor for blue). This clothlet was then wet with a binder and painted directly onto the parchment like a watercolor (Thompson, 1936).

1.3 MANIZOLA ANTIPHONARY 116C

Figure 6: Left, front cover. Right, *f.7r.*
Images © BPE and HERCULES Lab

The manuscript studied within this project is Antiphonary 116c of the Manizola collection, housed in the Biblioteca Pública de Évora (BPE). The library, established in 1805, houses numerous collections of historical importance. The Manizola collection includes 667 books dating from the 15th to 19th centuries and includes many varieties of documents including a Manueline *foral* charter, as well as scientific, historical, and religious texts (Silva, Martins, & Ferreira, 2010). This collection was willed to the BPE by the Visconde da Esperança, José Bernardo de Baraona Fragoso Cordovil Gama Lobo (1841-1931), having been housed previously within the Quinta da Manizola, near Évora (Vaz, 2007). The antiphonary, dating to the 16th century, was part of the inventory of the São Bento do Cástris monastery at the time of its closure in 1890. While the manuscript contains no indication of where it was originally commissioned, nor where it was produced, its presence in the monastic library, as well as the presence of iconography pointing toward an association with St. Bernard of Clairvaux and the Cistercian Order, makes it likely that the manuscript was made for the female Cistercian monastery, located just outside of Évora (Conde & da Silva, 2015).

An antiphonary (also called an antiphonal or antiphoner) is a type of choir book used in Catholic liturgy. As such, they tend to be large books that can be read with ease from a distance (Brown, 1994; De Hamel, 1986). Manizola 116c measures approximately 550 mm by 390 mm and is bound in embossed leather-covered wooden boards (Figure 6). The folia are an average size of 515 mm by 365 mm and are likely made of calf skin rather than that of sheep or goat, due to this large size (Thompson, 1936). Specific investigation of the hair follicles on the surface of the parchment, as is done by the IDAP Project, could give a more definitive identification of the source. The manuscript currently contains 62 folia, though there were likely 65 originally, with page numbers written on the upper right corner of the recto pages. These page numbers are not completely accurate, as a number of these notations were accidentally skipped or mislabeled. Any such error in numbering that may cause confusion within this work will be clarified as necessary. A full description of the organization and integration of folia within the manuscript is available in the codicological analysis by Conde and da Silva (2015).

Figure 7: *f*.4r, depiction of St. Bernard of Clairvaux
Image © BPE and HERCULES Lab

The manuscript contains 122 miniatures, all but one of which are decorated initials. This exception is the image of St. Bernard of Clairvaux on *f*.4r, supporting the manuscript's provenance (Figure 7). Another religious figure, incorporated into an initial, is found on the first page of the manuscript and depicts the Christ Child as *Salvator Mundi*. The rest of the initials fall into two main categories: those depicting plain capital letters on a decorated ground and those that incorporate anthro-and phytomorphic figures into the stylized initial. Two miniatures have been cut out, one from the second to last page of the manuscript and the second from *f*.13, which was later patched and the verso filled in with the missing musical notation. In addition to the miniatures, there are 87 calligraphic initials throughout the manuscript, drawn in black ink and surrounded by red or blue ink stippling or cross-hatching.

1.4 RESEARCH DESIGN

This work comprises two parts: the main being the identification of materials used in the production of Manizola 116c using a variety of spectroscopic and microscopic techniques and secondly, the preparation of lake pigments and paint mixtures based on historical documentation and recipes. These can be used as references to aid in the identification of similar components within the manuscript, either anticipated based on historical documentation and visual analysis or created experimentally in response to unclear or complicated results. By creating organic pigments rather than sourcing them commercially, they are sure to have been made in an historically relevant manner with, for instance, the substrates and extraction processes appropriate to the time studied, which may impact spectroscopic results.

Before extensive analysis of the manuscript is done, it must be visually analyzed. While material identification is the main concern of this work, optical and digital microscopy is first step to explore the methods utilized in the creation of the miniatures, as well as their conservation state. By observing the style and application of paint, in addition to its composition, a more holistic view of the production of the manuscript can be gained, allowing future researchers to better place the manuscript within a larger historical context.

Colorimetry is also used to accurately measure the colors found within the manuscript. This is a technique uses CIE L*a*b* Space, a common measurement standard designed by the Commission Internationale de l'Eclairage. Using a spectrophotometer, the color can be defined as coordinates and plotted to quantify and differentiate colors, even those with almost imperceptible differences (Artioli, 2010). While this technique can be used to correlate pigments to one another, it is also an excellent long-term conservation tool to monitor color degradation due to age or environmental exposure (Johnston-Feller, 2001).

In order to gain a comprehensive understanding of the palette and techniques utilized within this manuscript, a variety of complementary spectroscopic methods are employed, including those that require micro-sampling. As explored by Clarke, there are difficult choices to be made in planning whether or not to sample a manuscript. Because paint layers in manuscripts are usually very thin and cover a relatively small area, unlike in easel paintings or other painted surfaces, it is often seen as unacceptable to remove samples (2001a). The lack of sampling, however, can limit the information gained from the object. There are a number of *in situ/*non-invasive methods with which to analyze an object, yet they all have some drawbacks or limitations.

XRF is a portable technique widely used throughout the field of conservation and cultural heritage preservation. This elemental technique is quick and non-destructive, however it is only useful for heavier elements (sodium being the lightest) and cannot identify organic materials. This method can result in some complications, as happened in this work, due to the potential for results coming from X-rays penetrating further within the material than intended.

One method which has been increasingly utilized in the study of illuminated manuscripts is fiber optic reflectance spectroscopy (FORS). This technique is a form of UV-VIS-NIR spectroscopy, the wavelengths depending on instrumentation, which utilizes fiber optics to identify materials via their electronic transitions and molecular vibrations. While characteristic spectral features for many pigments have been documented and are available, it is common to create in-house paint samples with which to interpret one's results (Aceto, Agostino, Marcello, & Delaney, 2014). This method can be used to identify organic pigments; however, it is very difficult to identify composition in the case of paint mixtures. The instrumentation available for this project is limited to the visible and low-NIR regions and is unable give information about binders, which require NIR and IR frequencies to be identified properly (Ricciardi, et al., 2012).

By taking a conservative number of micro-samples (chosen based on the results from *in situ* analyses), more definitive information can be gained, especially in the case of complex or unclear results from non-destructive testing. Raman microscopy can be used *in situ*; this isn't an ideal method applied to manuscripts, as the laser tends to heat the parchment creating movement and loss of focus or, worse, potentially burn through the parchment and induce degradation processes in the surrounding areas (Aceto, et al., 2012). This is, regardless, not a possible option in the case of Manizola 116c due to its large size and the available instrumentation.

The presence of organic materials such as lake pigments will fluoresce and overwhelm the Raman shifts of other potentially identifiable materials (Bisulca, Picollo, Bacci, & Kunzelman, 2008). This effect can be minimized with adjustment to laser wavelength or the use of Surface Enhanced Raman Spectroscopy (SERS), in which noble metal substrates are applied to a sample to enhance the Raman signals (Whitney, Van Duyne, & Casadio, 2006). By not utilizing this technique, however, and taking the fluorescence simply as an indication of the presence of organic materials to be further investigated elsewhere, the samples can be reused using other techniques, thus minimizing the number of samples taken from the manuscript and maximizing the potential information to be gained.

FTIR and SEM-EDS complete the analytical techniques used with micro-sampling. FTIR can further confirm the presence of different pigments and mixtures, as well as being the only technique able to identify binders, due the aforementioned wavelength limitations of the available FORS instrument. In addition to confirming information gained from XRF analyses, SEM-EDS analysis can give morphological information about the pigments and gilding, as well as a better understanding of the trace elements found in organic materials (Kirby, Spring, & Higgitt, 2005).

This project aims not to identify every single pigment and material present, but to gain an understanding of the overall palette, by choosing areas that are both representative of those found throughout the book and best suited to the techniques utilized. Some materials, such as binders, can only be identified in a small number of samples. Similarities within the results from said samples, as well as those gained from the extensive FORS analyses, can be extrapolated to indicate larger trends within the production of the manuscript.

2. MATERIALS AND METHODS

2.1 LAKE PIGMENT PREPARATION AND PAINT STANDARDS

A variety of lake pigments were produced using recipes adapted from historic sources. The red lake pigments include those produced from cochineal, madder, and brazilwood. Yellow lake pigments were created from weld and unripe buckthorn berries (ground).

All inorganic pigments and dyestuffs used were purchased from Kremer Pigmente. Parchment glue, glair, egg yolk, and arabic gum binders were produced in the lab. The egg-based binders were produced using chicken eggs. The arabic gum was also sourced from Kremer Pigmente and was prepared in a 10%/wt solution in water. Water used in these preparations was treated using a Millipore Simplicity UV system.

The paint swatches were applied on parchment acquired from Museé du Parchemin, (Rouen, France) and were created using 4:1 binder to pigment mixtures (based on dry weight). Each binder had its own paintbrush and pipette to minimize contamination. The paints were mixed on watch glasses with an agate or ground glass pestle and washed thoroughly with dish soap between mixing to minimize contamination.

2.1.1 COCHINEAL LAKE PIGMENTS

The recipe followed for all cochineal dyes and lakes comes from that developed for the CHARISMA Project *Back to the Roots* 2011 workshop and is based on a 15th century Italian recipe no. 110 from ‘Segreti per colori’ or the Bolognese Manuscript (Merrifield, 1849).

2.1.1.1 COCHINEAL LAKE #1

0.262 g alum ($AlK(SO_4)_2 \cdot 12H_2O$) and 0.131 g sodium tartrate ($Na_2C_4H_4O_6$. Used as a substitute for potassium bitartrate, or ‘cream of tartar’, which could not be procured) was added to 131 mL of water. This solution was brought to 40°C. 1.31 g of undyed wool yarn was added to the solution, heated to 95°C and kept at this temperature for 45 minutes. The solution allowed to cool and the wool was rinsed with water.

0.131 g ground cochineal was added to 300 mL water and heated to 40°C. The mordanted wool was added, heated to 80°C for 60 minutes while stirring. The wool was then rinsed until the water ran clear and was left to air dry.

The dyed yarn was cut into fine clippings approximately 3 mm in length and added to 52 mL 0.1 M K_2CO_3 solution. This was heated to 60°C. The recipe suggests boiling the solution for 10-15 minutes (Or 30-40 minutes at a lower temperature) in order to remove all the color from the wool, however after boiling for 15 minutes, the wool still retained much of the dye. The temperature was lowered to 50°C and kept at this temperature, while stirring, for one hour. The solution was filtered using a Whatman 114 paper to remove the fibers and reheated to 50°C. A solution of 1.574 g alum and 7.9 mL water, heated slightly to dissolve, was slowly added to the dye solution, still stirring, until the effervescence stopped. This was then covered and left overnight. The next day, the precipitate was filtered using a Buchner funnel and Whatman 114 filter and left to dry in a desiccator. This recipe produced a purple lake pigment.

2.1.1.2 COCHINEAL LAKE #2

A modified version of the above recipe was used for the second attempt, utilizing the updated recipes in the book published from the CHARISMA project (Kirby, van Bommel, & Verhecken, Natural Colorants for Dyeing and Lake Pigments: Practical recipes and their historical sources, 2014). The same overall method was used using the following amounts:

Mordant:
2 g wool, 0.4 g alum, 100 mL H_20
Dye:
0.2 g cochineal, 73 mL H_20
Lake Preparation:
2 g alum, 10 mL H_20, 60 mL 0.1 M K_2CO_3

The amount of water used during the dye process was reduced considerably, as the amount used in the first attempt was found to be a conversion error. However, the wool was very confined within this small amount of liquid. The temperatures were kept low throughout the process, never allowed to rise above 60℃, in an attempt to see how temperature affected the resultant color.

2.1.1.3 COCHINEAL LAKE #3A-B

The same was repeated as in Cochineal #2, but added the 0.214 g of sodium tartrate as in the first recipe. The amount of water during the dyeing process was increased to 500 mL. The resulting yarn was red as expected. Before precipitating the lake, the solution was separated into two 26 mL portions. Commercially obtained white vinegar was added dropwise to each to see how the color changed in relation to pH. Cochineal #3a received 40 drops from a glass Pasteur pipette, while Cochineal #3b received 100. This successfully turned the solutions red, but the resulting lakes were dark, coarse, and still quite purple.

2.1.2 BRAZILWOOD LAKE PIGMENT

The CHARISMA Project recipes were again used to create the brazilwood lake. The recipe is adapted from the Bolognese Manuscript, recipe B 136, and originally would have been referring to sappanwood (Merrifield, 1849).

40 g of brazilwood, ground in a coffee grinder, was added to 1300 mL water and heated until the solution had reduced by to approximately 650 mL. The solution was filtered to remove the plant matter. 25 g alum was dissolved in 200 mL water and added to the dye solution. A solution of 20 g potassium carbonate and 100 mL water was slowly added to the previous solution, stirring, until effervescence stopped. This was covered and left to sit overnight. This recipe produced an incredible amount of product and would have been too time consuming to filter it all. It was separated into small plastic containers and lyophilized for four days until all the liquid was removed. The contents of 2 containers out of 29 (all with varying amount of liquid and precipitate, so a final yield cannot be determined) were further rinsed and filtered with a Buchner funnel and Whatman 114 paper.

2.1.3 MADDER LAKE PIGMENTS

2.1.3.1 MADDER LAKE #1

This recipe was again from the CHARISMA Project, a 15th century German recipe originally sourced from E.E. Ploss, Ein Buch von alten Farben: Technologie der Textilfarben im Mittelalter mit einem Ausblick auf die festen Farben, Heidelberg and Berlin 1962, the Nuremburg Kunstbuch (15th century) pp. 113–14.

A mordant called ‘semelwater’ was created using 20 g of wheat bran was added to 450 mL of water and brought to a boil. It was removed from the heat and 300 mL more water was added and the container was covered. The first day, this liquid was stirred every hour, totally 7 repetitions. It was left to sit and after 6 days, 400 mL was removed and replaced with 400 mL of fresh, hot water. It was stirred once more and left 24 hours (Hacke, 2006).

0.75 g alum was added to 250 mL of the above semelwater and dissolved. 5 g of undyed wool yarn was added to this solution and boiled for 2 hours, after which the yarn was drained, but not wrung out. 3 g of madder was added to 100 mL semelwater and 150 mL water. Stirring, this was brought to 40°C. The mordanted wool was added and kept at 90°C for 3 hours. The yarn was then drained, rinsed, and wrung out before being placed for 30 minutes into a solution of 0.5 g K_2CO_3 and 250 mL water. The yarn was rinsed again and left to dry.

The recipe to create a lake pigment from the dyed yarn is different from the other recipes used in this project, as it attempts to use an alkaline solution to break down the fibers of the wool into a “jelly” and use this as the body of the pigment (Kirby, Spring, & Higgitt, 2005; Kirby, van Bommel, & Verhecken, 2014). This was unsuccessful and detailed fully below. Please see Appendix I.1 for the full recipe.

2.1.3.2 MADDER LAKE #2

The second attempt utilizes a recipe that bypasses the dyeing stage and attempts to extract color directly from the madder. 2 g of ground madder was placed in a polyester bag and soaked overnight in 60 mL water. This was then heated to 70°C for 30 minutes. The bag was removed and the liquid was poured through a filter to remove any remaining plant matter. 1 g of alum was added to the solution and heated to 80°C. Separately, 0.4 g K_2CO_3 was dissolved in 40 mL water. The dye solution was slowly added to this, stirring constantly. It was filtered and washed the next day and left to dry in a desiccator (Kirby, van Bommel, & Verhecken, 2014).

2.1.4 WELD AND BUCKTHORN LAKE PIGMENTS

The weld and buckthorn lakes were produced using the same recipe. 2 g of dyestuff was added to a polyester bag and placed in 120 mL water. The next day, it was boiled for 30 minutes while stirring. The bag was removed and the liquid was filtered to remove excess plant matter. 2 g K_2CO_3 was added to this and heated to 80°C. A solution of 6 g alum in 30 mL water is created by heating and returning to room temperature. This solution was gradually added to the dye solution, while stirring, until effervescence stopped. The precipitate was left to settle and was filtered, rinsed, and dried in a desiccator. (Kirby, van Bommel, & Verhecken, 2014)

2.2 ANALYTICAL TECHNIQUES

2.2.1 OPTICAL AND DIGITAL MICROSCOPY

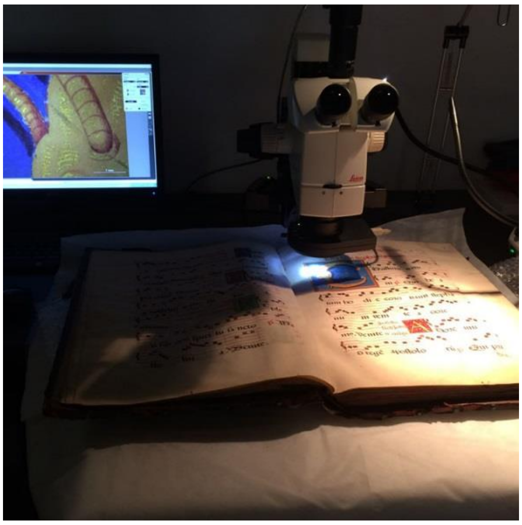


Figure 8: The manuscript under the stereomicroscope. This shows the maximum distance possible to observe under the microscope.

Due to the large size of the antiphonary to be analyzed, two types of equipment were used. First, observations were made using a Leica M205C stereo microscope. (Figure 8) Images were taken with the attached Leica DFC295 camera and Leica software application suite (LAS) at 1-4x magnification. All other images were taken using a Dino-Lite Premier AM7013MZT4 digital handheld microscope at 430-435x magnification using the DinoCapture 2.0 software.

2.2.2 FIBER OPTIC REFLECTANCE SPECTROSCOPY

FORS analysis was made using an ASEQ Instruments LR1-T v.2 compact spectrometer, with a spectral range of 300-1000 nm and a spectral resolution of <1 nm (with 50 µm slit). Measurements were taken using the ASEQ CheckTR software. Calibration was made using Whatman filter paper. Samples were analyzed at an exposure of 100-200 ms, 5 scans, and a BoxCar smoothing of 15. Each spot was measured three times for 5 seconds each.

2.2.3 COLORIMETRY

Colorimetric data was collected using a portable Datacolor Check II Plus spectrophotometer. This instrument has diffuse illumination 8° viewing in conformance with CIE publication No. 15.2 Colorimetry. It uses a pulsed xenon light source, a spectral range of 360-700 nm, an effective bandwidth of 10 nm, and a wavelength bandwidth of 2 nm. It was calibrated using the accompanying white and black calibration accessories. Analysis was made with measuring times <2.5 seconds with an aperture spot size of 3 mm. Each sample was analyzed three times to create an average and identify variations within the painted areas.

2.2.4 X-RAY FLUORESCENCE SPECTROSCOPY

XRF analysis was done using a Bruker Tracer III-SD handheld X-ray fluorescence spectrometer. It has a 10 mm^2 XFlash® SDD; peltier cooled detector with a typical resolution of 145 eV at 100,000 cps. It has a Rh target X-ray tube and a maximum voltage of 40 kV.

Analysis was made using 40 kV, 12.5 μA current, Al/Ti filter (304.8 μm aluminum/25.4 μm titanium), and an acquisition time of 90 seconds. The instrument was fixed in place using a tripod and positioned approximately 2-3 mm away from the surface of the page. A sheet of plexiglass (~3 mm thick) was placed behind each working area in order to minimize results from further within the manuscript. Spectra were collected using the S1PXRF software and analyzed using ARTAX.

2.2.5 MICRO-RAMAN SPECTROSCOPY

μ-Raman microscopy was done with an XPlora Horiba Jobin Yvon Raman spectrometer and an Olympus BX41 microscope. This instrument is equipped with both a 638nm (17 mW) and a 785 nm (24 mW) laser and were focused using 10x, 50x, and 100x objective lenses. The analyses were done with a filter of 0.1-10% and acquisition times ranging from 5-20 s depending on each sample. The spatial resolution is approximately 4 μm. Spectra were collected using the LabSpec 5 software and compared with spectral databases.

2.2.6 MICRO-FTIR

μ-FTIR analysis was completed using a Bruker Hyperion 3000 infrared spectrometer equipped with a single point MCT detector cooled with liquid nitrogen. A 15x objective lens was used. The spectra were collected in transmission mode, in 50–100 μm areas, using a S.T. Japan diamond anvil compression cell. The infrared spectra were acquired with a spectral resolution of 4 cm^{-1}, 32 scans, in the 4000-650 cm^{-1} of the infrared region.

2.2.7 SEM-EDS

Eight pigment microsamples were analyzed with a variable pressure scanning electron microscope Hitachi S-3700N. Chemical composition was determined with a Bruker EDS XFlash 5010 Silicon Drift Detector energy dispersive X-ray spectrometer. The resolution of the EDS detector is 123 eV at Mn Kα. The samples were mounted onto carbon tape and analyzed with an accelerating voltage of 20 kV and a chamber pressure of 40 Pa (uncoated samples). The EDS tasks were achieved through the Esprit1.9 software from Bruker Corporation.

2.3 SAMPLING AND ANALYSIS OF MANIZOLA 116C MANUSCRIPT

In situ analysis and sampling were done on 19 miniatures within the manuscript, as well as *in situ* analysis of the red and black inks of the text (Table 2). These images and areas were chosen because they afforded the largest areas of uninterrupted color, allowing for easier analysis using equipment with large spot sizes, as well as the widest variety of colors in order to gain a comprehensive understanding of the illuminator's palette.

A total of 13 micro-samples were taken from 5 miniatures for more extensive analysis. These samples were taken by a skilled researcher[1] with several years of experience in taking micro-samples. Sampling was limited to those areas within approximately 15 cm from the edge of the manuscript, due to the necessity of working under a standard microscope (Figure 8).

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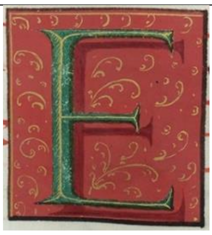
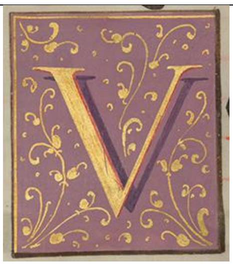
[1] Dr Catarina Miguel, of HERCULES Laboratory and co-supervisor of this thesis.

Table 2: Overview of pages and sizes of miniatures analyzed.
Underlined page numbers indicate the use of micro-sampling
Images © BPE and HERCULES Lab

 **_f_.7r** 119 mm x 117 mm	 **_f_.9v** 54 mm x 58 mm	 **_f_.13r-a** 52 mm x 55 mm	 **_f_.13r-b** 52 mm x 53 mm
 **_f_.13v-a** 60 mm x 68 mm	 **_f_.13v-b** 60 mm x 68 mm	 **_f_.13v-c** 57 mm x 58 mm	 **_f_.14v** 37 mm x 47 mm
 **_f_.15v** 38 mm x 44 mm	 **_f_.31r** 112 mm x 120 mm	 **_f_.33r** 100 mm x 107 mm	 **_f_.35r** 87 mm x 107 mm
 **_f_.37v** 93 mm x 105 mm	 **_f_.39*r** 89 mm x 107 mm	 **_f_.41b** 93 mm x 106 m	 **_f_.42v** 120 mm x 116 mm
 **_f_.48v** 42 mm x 54 mm	 **_f_.50r** 40 mm x 52 mm	 **_f_.53v** 44 mm x 51 mm	 

3. RESULTS AND DISCUSSION

3.1 LAKE PREPARATION AND PAINT STANDARDS

Figure 9: Prepared Lake Pigments. L-R, Weld, Buckthorn, Madder, Brazilwood, Cochineal 1, 2, 3A, and 3B

Five types of lake pigments were created for this project: brazilwood, madder, cochineal, weld, and buckthorn (Figure 9). While these recipes were adapted by Kirby, et al. (2014) to account for modern weights and measurements, there were some issues in terms of yield and success in pigment creation. As stated previously, the brazilwood lake in particular produced far more product than anticipated, but was successful in every other way. Upon this realization, the subsequent lake pigment recipes were scaled back, especially as there were limitations in lab space and equipment. However, the final yields of the lake pigments sourced from dyed wool produced comparatively very little, limiting the amount of experimentation in terms of pigment mixtures for test swatches.

Figure 10: Cochineal Lake Pigment Process

The results of the cochineal lake preparation gave a very purple color as opposed to the red the dyestuff is known for (Figure 10). This is due to the nature of some chromophores, specifically anthraquinones such as carminic acid, being able to shift in color depending on their pH; historic treatises mention the addition of a variety of reagents in order to gain specific colors from such dyestuffs (Clarke M. , 1999; Merrifield, 1849). Simply in the interest of understanding more about how these colors are affected, more attempts were made to create a cochineal lake with a redder hue, though only one historically appropriate recipe could be found with modern measurements. Literature suggests that lower temperatures during the dyeing and lake preparation processes can create redder colors (Kirby, van Bommel, & Verhecken, 2014). This was attempted in Cochineal Lake 2 which resulted in a very dark purple wool and a lake pigment that, while not the rich red traditionally associated with cochineal, was redder than the previous attempt. In Cochineal Lakes 3a and 3b, distilled vinegar was added before precipitation. This successfully turned the solution a dark red and the resulting pigment a reddish purple, but it was very dark and far more difficult to grind and mix with binders than the previous attempts. It is likely that to create a bright red lake from cochineal, one must utilize acidic reagents early in the process, such as the recipe found in the 17th century Paduan Ms. which calls for the boiling of cochineal with lemon juice, garlic juice, and burnt alum (Merrifield, 1849). All of these lake pigments showed the same FORS spectra, which also matched that found in literature, therefore no further experimentation was necessary.

Figure 11: Left, Wool yarn dyed with madder.
Right, a microscopic photo of the results of the first madder lake

Attempts to create madder lakes were largely unsuccessful. The first attempt utilized a recipe (converted for modern use) that followed a method very common for this type of dyestuff: the dye was not extracted from a textile, but rather the fibers were broken down in an alkaline environment and utilized as the body of the subsequent lake pigment (Kirby, van Bommel, & Verhecken, 2014). While this recipe has been used successfully by Kirby et al., it was ultimately unsuccessful here. The alkaline solution (potassium carbonate) was to be tested until it was strong enough to allow for the barbs of a feather to be easily stripped from its quill. However, the concentration of the solution had to be tripled before it showed even marginal success. The breakdown of the wool fibers was incomplete in the first attempt and, upon filtering and drying, it was clear that it was unsuitable for use as a pigment (Figure 11).

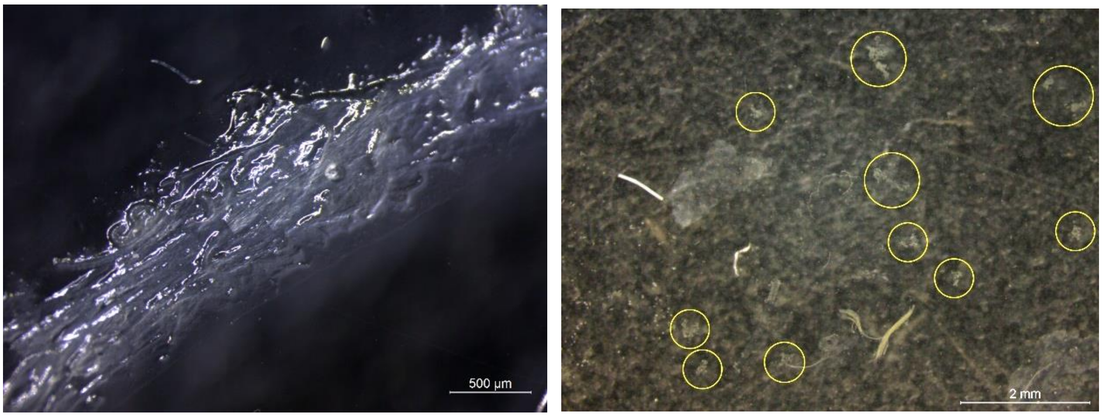


Figure 12: Left, first attempt to reduce undyed wool to jelly. Intact wool fibers show that this process was unsuccessful. Right, solution of wool that was successfully broken down. Yellow circles indicate the supposed "jelly" the recipe describes.

More experimentation was done in attempting to break down wool into "jelly" by using undyed wool. It appears that the issue comes from having scaled down the recipe. Due to the lack of space and equipment in the lab, only 5 g of dyed wool yarn was used instead of the 40g called for in the recipe. Using undyed wool, the recipe was followed until, after 7 hours, it appeared that there was only a "jelly" and no longer any wool fibers. However, under the microscope, it was clear that this was not the case and the "jelly" had been misidentified (Figure 11). A second attempt was made using the tripled concentration (0.9 M K_2CO_3). After 7 hours of boiling, stirring, and adding water frequently to make sure it did not dry out, the solution finally became clear. Upon viewing the solution under a microscope, small transparent clumps were visible (Figure 12). These appear to be the "jelly" the recipe is calling for and that such a small amount of wool is incapable of producing enough to make a sufficient amount of pigment.

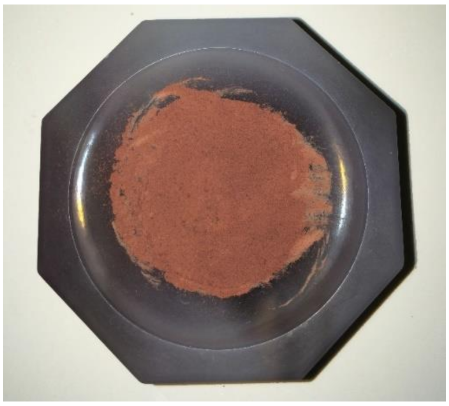


Figure 13: Brownish madder lake pigment

A second attempt at a madder lake was completed using a recipe that called for the extraction of dye from the plant itself, rather than through a dyed textile intermediate. While the process appeared to proceed as expected, the final pigment appeared a dull and brownish pink (Figure 13). Furthermore, the FORS spectra of the resulting paint swatches do not match that described in the literature. It is possible that this is due to insufficient steeping time and not enough of the dye was extracted. It is unlikely that there is an issue with the dyestuff used, as the previous attempt utilizing more intense extraction and dyeing methods resulted in richly colored wool yarn. Paint swatches using a previously prepared madder lake pigment[2] based on a 19th century recipe, however, did produce the expected FORS spectra and were used instead as standards.

Weld and buckthorn lakes were prepared after having identified an unknown organic yellow pigment within the manuscript. These were both created using direct extraction methods similar to that used in the second madder lake attempt discussed above, however these were successful.

---

[2] Prepared by HERCULES researcher, Ana Manhita.

Table 3: Paint reference samples
Binders used, unless specified, L-R: parchment glue, egg white, egg yolk, arabic gum

<table>
<tr><td colspan="3"></td></tr>
<tr><td>Brazilwood Lake</td><td>Yellow Ochre</td><td>90:10%wt, Azurite : Smalt</td></tr>
<tr><td>Cochineal Lake #1</td><td>Weld Lake</td><td>90:10%wt, Azurite : CaCO$_3$</td></tr>
<tr><td>90:10%wt,
Vermilion : Red Ochre</td><td>90:10%wt,
Weld Lake : Yellow Ochre</td><td>Madder Lake (brown)</td></tr>
<tr><td>90:10%wt, Vermilion : Minium</td><td>Buckthorn Lake</td><td>90:10%wt,
Lake Cochineal #2 : CaCO$_3$</td></tr>
<tr><td>90:10%wt, Vermilion : CaCO$_3$</td><td>90:10%wt,
Buckthorn Lake : Yellow Ochre</td><td>90:10%wt,
Cochineal Lake#2 : CaSO$_4$</td></tr>
<tr><td>90:10%wt, Vermilion : CaSO$_4$</td><td>Cochineal Lake #2</td><td rowspan="2">Cochineal #1 and #2 in arabic gum only, 0.24 g and 0.4 g</td></tr>
<tr><td>90:10%wt, Vermilion : Lead White</td><td>Cochineal Lake #3a</td></tr>
<tr><td>Madder Lake</td><td>Cochineal Lake #3b</td><td rowspan="2">Cochineal #1 in egg white only, 4:1, 3:1, 2:1 ratio by wt binder to pigment.</td></tr>
<tr><td>90:10%wt,
Vermilion : Cochineal Lake #1</td><td>90:10%wt,
Azurite : Lead White</td></tr>
</table>

In addition to the lake pigments alone, a number of mixtures with inorganic pigments and extenders were painted on parchment using different historically relevant binders (Table 3). Each were mixed in a 4:1 ratio by weight of binder to total pigment and applied in three layers in order to evenly coat the surface of the parchment. These paint samples were all analyzed with FORS to gain a better understanding of how these mixtures affect the spectra and whether or not it is possible to differentiate between them, especially in instances with a very imbalanced mixture, such as 90/10 wt%. Colorimetric analysis was completed for all the paint samples. (Please see Appendix I.2 for these results.)

3.2 MATERIAL ANALYSIS OF MANIZOLA 116C

3.2.1 VISUAL AND MICROSCOPIC ANALYSIS

Figure 14: Detail photographs of *f*.35r, *f*.7r, and *f*.50r.
Images © BPE and HERCULES Lab

The images in Manizola 116v are highly sophisticated. In every miniature, even the most basic capital, there is a three-dimensionality created through a number of techniques. Shadows are used to create the sense that each letter or figure is hovering just above the background (Figure 14). The forms of each figure are given shape by finely detailed hatching, primarily in white or gold, to enforce a sense of volume.

Figure 15: f.33r, the effect of light on the gilding
Images © BPE and HERCULES Lab

In some letters entirely composed of gold, such as that on *f*.50r, different colors of gold are used to further create volume within the letter. Gold is used extensively throughout the manuscript in the background in the form of filigree and fish-scale patterns, as well as within the figures. This use of gold, painted on rather than laid down in the form of gold leaf, brings light into the manuscript and creates a dynamic experience for the viewer, allowing the shapes to jump from the pages as they are turned or as the ambient light changes (Figure 15).

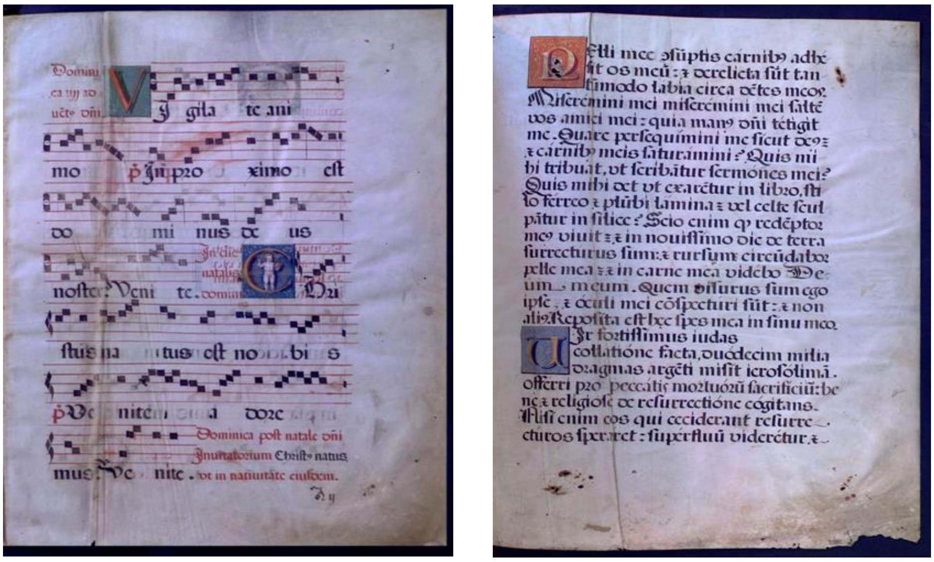


Figure 16: The first and last pages of the manuscript
Images © BPE and HERCULES Lab

The miniatures found within Manizola 116c are in a relatively good state of conservation. The majority of them are intact and do not exhibit any flaking or extensive cracking. The most extensive damage appears in areas of creased or rumpled parchment, the worst of this damage found on the first and last pages of the manuscript. The latter has holes eaten through the parchment itself in areas corresponding to the corrosion from the metal studs on the lower board (Figure 16).

Figure 17: Left, *f*.42v Pigment loss due to abrasion. Right, *f*.15v Unidentified pigment loss
Images © BPE and HERCULES Lab

Other forms of damage to the miniatures include what appears to be pigment loss due to abrasion. Two such areas of loss, the face of a grotesque figure on *f*.42v and a skull on *f*.46r, appear to have been purposefully rubbed away (Figure 17). Areas of erasure like these are frequently found within medieval manuscripts, especially in depictions of demonic or obscene entities, likely as a way for the reader to protect themselves from the potentially malign gaze (Camille, 1998). The cause of damage due to abrasion elsewhere in the manuscript is more difficult to interpret. In the miniature on *f*.41v, an area of the gold scale-like patterning is missing, exposing the yellow background below. Under a microscope, this area does not appear to be overpaint, as there is no clear edge to the abraded region and the paint layers appear to have the same texture and stray dispersed pigments (Figure 18).

Figure 18: Left, *f*.41v Area of gold pigment loss circled.
Right, microscopic image of intact (a.) and abraded (b.) areas.
Images © BPE and HERCULES Lab

The majority of damage occurs within white crosshatching highlights which consistently contain cracks. These highlights have a glossier finish than the rest of the painted areas. This is likely due to the type of binder used here. As stated previously, a glossy finish could be achieved through the use of arabic gum and honey or the addition of a small amount of egg yolk to glair, which gives it body and luster (Thompson, 1936). This change in texture is not clearly visible to the viewer, though it may make the highlights stand out more, and it is likely that it was done to create more control for the artist. These lines require precision to achieve their intended effect and thin paint that ran or absorbed into other areas would not allow the underlying forms to be read correctly. The same apparent mixture is also used in larger areas such as on the chest of the figure on *f*.41v (Figure 19). This type of degradation has been well-documented as frequently occurring in lead white, due to its chemical interaction with binders and accelerated drying properties (Centeno, Guzman, Yamazaki-Kleps, & Della Vedova, 2004; Lawson, 2008).

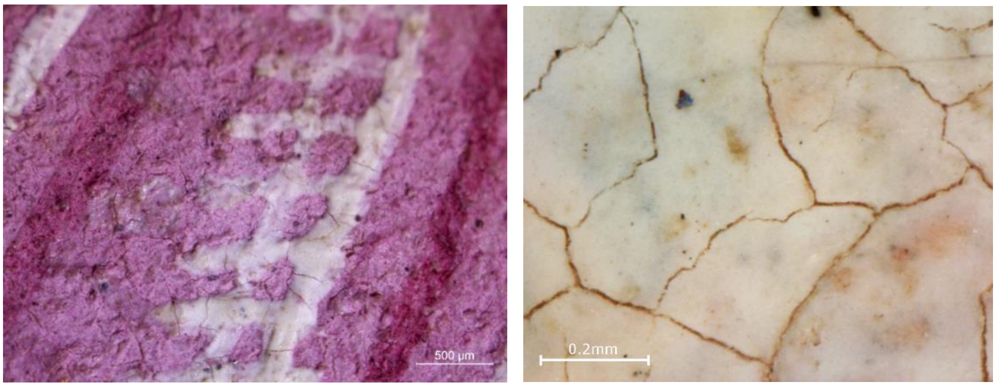


Figure 19: *f*.41v, Detail of cracking throughout white painted areas
Left, a microscopic image of crosshatching on the tail of the main figure
Right, an image of the white paint layer on the chest of the figure, taken with a digital microscope.

While the majority of the miniatures in the manuscript are very similar, appearing to have been painted by the same person, there are a number that appear to have been created less skillfully or deviate from standard established layouts. Aside from judgements of artistic skill, a clearly identifiable variation is found in the borders of the miniatures. Throughout the majority of the manuscript, two types of borders are seen: a brown border modeled in complementary shades and gold stripes to create an illusory frame, and a plain black line (Figure 20).

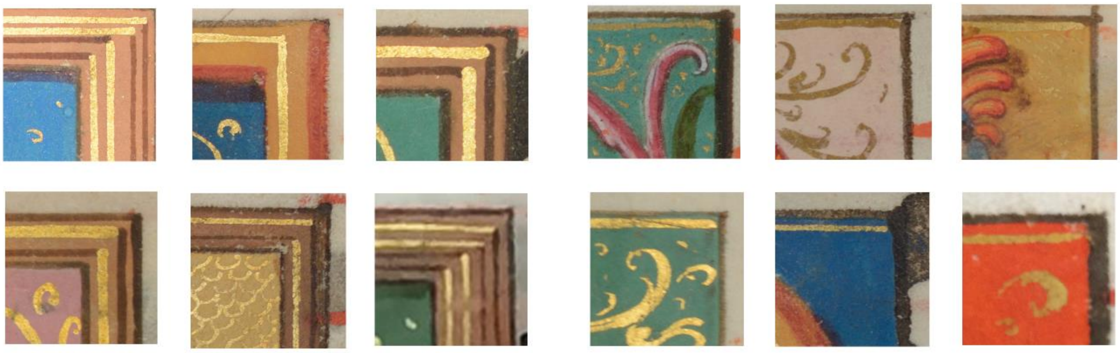


Figure 20: Photographic images showing comparison of border styles.
Left, Clockwise from top left: *f*.7, 33, 35, 39, 41, 42
Right, Clockwise from top left: *f.13r*, 13v a-b-c, 14v, 48v

A number of other miniatures, such as those on *f*.9v, *f*.31r, and *f*.37v, have different types of borders, which appear to be painted over previous work. The image on *f*.9v, is bordered by a wide, pale purple frame (Figure 21). The color alone is unusual, but it is also far thicker than other applications of paint found throughout the manuscript, with no visible texture of the underlying parchment. When removing a micro-sample from this area, it also appeared to be very powdery, as though it did not have enough binder. This is in contrast to other areas of sampling in which it was more difficult to remove pigment from the surface of the parchment. While powdery and crumbling when disturbed, the area is relatively cohesive with no major areas of loss.

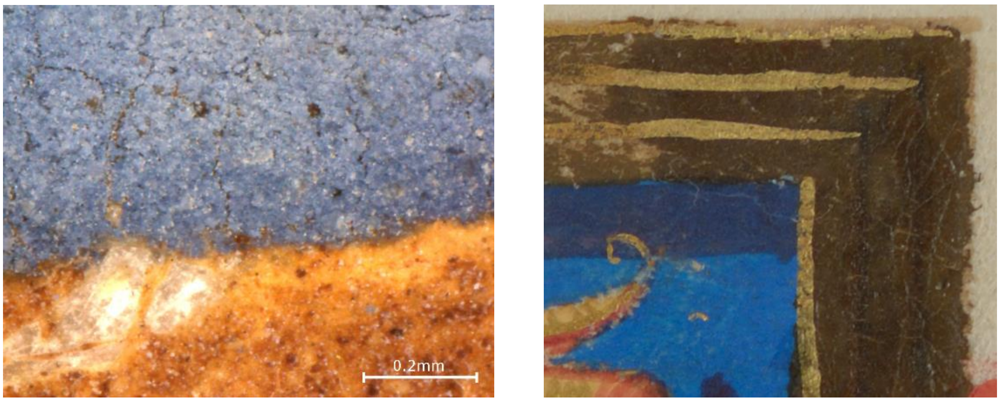


Figure 21: Left, microscopic image of *f*.9v border. Right, photographic image of *f*.31v border.

The border of the image on *f*.31r does follow the overall design of the other brown-framed miniatures, but has been applied in a much thicker and less skillful way (Figure 21). The surface of the paint is cracking, textured, and worn away in ways that are not seen throughout the rest of the manuscript. Under close inspection of the right side, underlying lines are visible beneath the paint layer. The miniature itself, as well as that on *f*.37v, is not very skillfully done when compared to others in the manuscript. The figures do not have the same precise crosshatching to create forms, relying more on washes of color. The crosshatching that is used in these miniatures is not very effective, creating more of a flat pattern rather than shape. The border of *f*.37v looks very similar to the standard brown frame borders, but is the only instance within the manuscript in which a figure overlaps its border. The background of this miniature is also the only instance of a completely gold background and is applied inconsistently with visible brush strokes (Figure 22).

Figure 22: Left, *f*.35r. Right, *f*.37v
Images © BPE and HERCULES Lab

It is unclear as to why these miniatures were painted later, as no underlying paint layer is visible. In the case of *f*.37v, the lines from the other side of the page are clearly visible through the image indicating a fairly thin application of paint. Occasionally manuscripts were left unfinished and it is possible that these areas were originally not filled in fully (Alexander J. J., 1992). They may have been completed later using the motifs found elsewhere within the manuscript as a guide, rather than painting directly over a previous image that had been damaged, but this cannot be confirmed without more invasive study. Depictions of insects such as caterpillars, beetles, and moths are only found within four miniatures, three of which are suspected to be painted later: *f*.8v, *f*.31r, *f*.37v, and *f*.39*r. The snail on *f*.39*r appears to be an original part of the composition as the gold background decorations appear to purposefully frame it.

Throughout the rest of the manuscript, the figures are modeled in a painterly way, not simply using cross-hatching to create volume, but through layers and transparent glazes. Layering of paints is most easily seen in the handling of bird feathers, such as those found on *f*.13v (Figure 23). In this area, lines of red and possibly blue are laid down on bare parchment over to which transparent blue is added, so that the lines below are visible. More colors are layered upon this, building up color and texture to better convey the sense of bird feathers. These transparent layers are also found creating shadows, sometimes overlapping areas of gilding, such as in *f*.53v which includes transparent layers creating shadows over both the background and the gold letter (Figure 23).

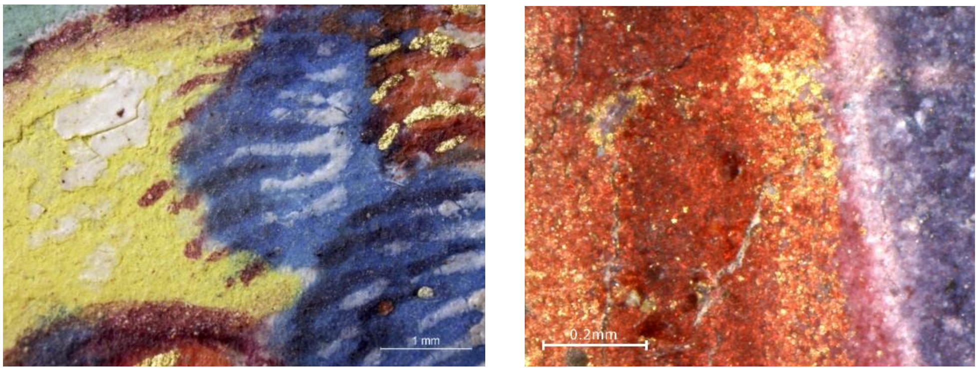


Figure 23: Left, optical microscopic image of bird in *f*.13v.
Right, digital microscopic image of transparent paint layers over gilding on *f*.53v

Finally, colorimetric results were taken of the analyzed miniatures, which give the exact color of each sampled area and can be used in the future to monitor any color change within the manuscript (Table 4). Please see Appendix II for specific locations of colorimetric analysis.

TABLE 4: COLORIMETRIC DATA FROM MANIZOLA 116C.

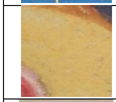
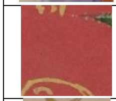
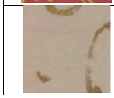
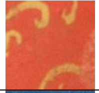
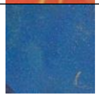
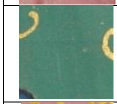
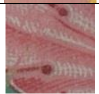
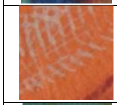
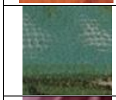
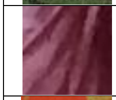
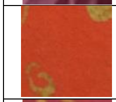
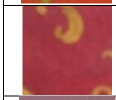
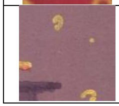
Average CIE L*a*b*				
	Folio - Color	**L***	**a***	**b***
	*f*.7r - Blue	37.83 ±2.06	-7.30 ±0.62	-24.69 ±2.68
	*f*.9v – Yellow	63.15 ±4.43	6.58 ±1.29	24.06 ±3.00
	*f*.9v – Purple	50.27 ±1.89	-0.03 ±0.07	-7.28 ±1.68
	*f*.13r – Red	43.77 ±1.43	31.06 ±1.07	17.03 ±0.74
	*f*.13v-a – Pale Pink	68.42 ±1.75	4.72 ±0.79	11.03 ±1.43

TABLE 4 CONTINUED : COLORIMETRIC DATA FROM MANIZOLA 116C

	*f*.13v-b – Pink	51.03 ±2.53	16.32 ±2.37	1.81 ±0.22
	*f*.14v – Blue	48.31 ±3.37	-9.04 ±1.56	-14.11 ±2.78
	*f*.15v – Red	46.32 ±1.55	31.44 ±4.31	24.66 ±3.20
	*f*.31r – Blue	42.16 ±3.99	-6.93 ±1.14	-26.83 ±1.5
	*f*.31r – Red	27.79 ±1.53	21.68 ±1.35	7.90 ±0.81
	*f*.33r – Bright Blue	33.61 ±1.29	-9.33 ±0.64	-13.73 ±1.49
	*f*.33r – Dark Blue	28.90 ±0.44	2.80 ±0.03	-4.23 ±0.35
	*f*.35r – Pink	51.96 ±1.29	25.45 ±0.79	2.26 ±0.16
	*f*.35r – Green	41.84 ±1.02	-16.35 ±0.1	5.86 ±0.06
	*f*.39r – Pink	50.90 ±1.01	15.53 ±0.7	3.55 ±3.3
	*f*.41v – Pink	43.03 ±1.02	10.45 ±1.36	2.18 ±1.86
	*f*.41v – Blue	42.66 ±2.78	-1.35 ±1.32	-5.42 ±1.77
	*f*.41v – Red/Orange	59.11 ±0.78	33.86 ±1.89	27.47 ±0.37
	*f*.41v – Green	47.6 5±2.2	-10.21 ±1.5	8.26 ±4.03
	*f*.42v - Pink	50.30 ±0.79	26.52 ±2.04	3.84 ±0.87
	*f*.48v – Red	52.94 ±1.01	33.26 ±3.76	27.31 ±0.42
	*f*.50r – Red	44.15 ±0.36	31.05 ±2.62	9.11 ±0.87
	*f*.53v - Purple	52.19 ±0.37	10.57 ±1.1	-3.37 ±0.42

3.2.2 PIGMENT IDENTIFICATION

Before delving fully into the identification of pigments, a clarification must be made regarding the XRF spectra obtained. While it is expected that XRF is not an ideal method for analyzing lake pigments, as only the metal substrate will appear, the XRF analyses done on this manuscript were particularly misleading, even in the case of inorganic pigments (Clementi, et al., 2008). Paint and ink from the other side of the folia were consistently picked up by the XRF instrument. Due to the large spot size of the instrument and how densely decorated the pages are, the majority of the results contain the same selection of elements, namely Hg, Fe, and Zn (from the red and black inks). In the few areas where there was nothing on the other side of the page, the spot analyzed was often too large for the area of interest and picked up surrounding pigments, especially due to the layering effects described above. Complementary techniques are frequently employed in the material investigation of art in order to gain a comprehensive understanding of the materials, however they were a necessity in this project as XRF spectra could often not be depended on to make definitive identification. Please see appendix for superimposed images (recto and verso).

3.2.2.1 RED

3.2.2.1.1 LAKE PIGMENTS

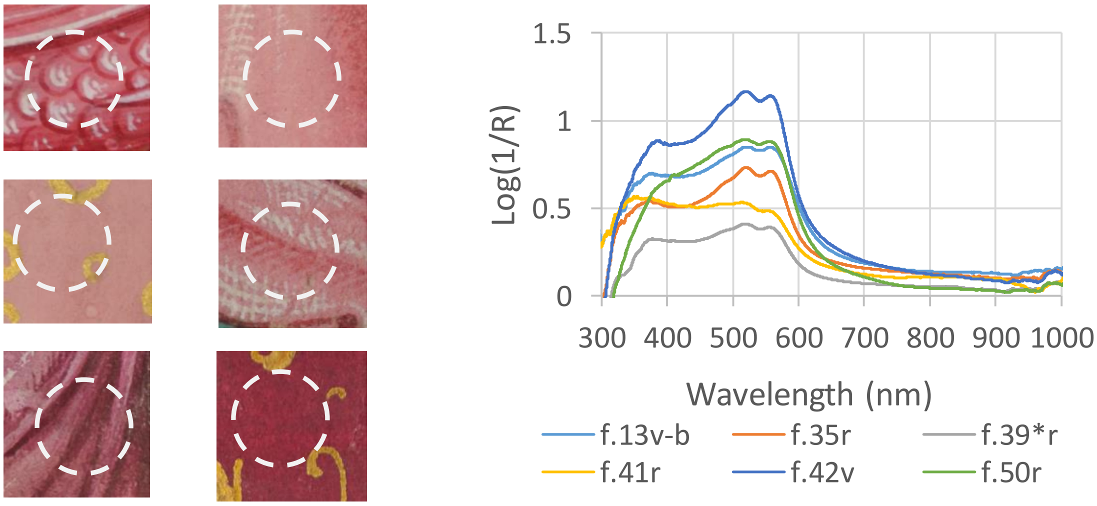


Figure 24: FORS Spectra of Pink/Red Organic Pigments.
Thumbnails indicating spot of analysis, top left: *f*.13v-b, 35r. Middle: *f*.39*r, 41v. Bottom: *f*.42v, 50r.

Use of organic pink and red paints can be found throughout the manuscript. Six miniatures were analyzed and found to contain lake pigments (*f*.13v-b[3], *f*.35r, *f*.39*r[4], *f*.41r, *f*.42v, and *f*.50r). The spectra obtained using FORS were treated with a log(1/R) conversion to obtain *apparent absorbance* spectra, in order to aid in the identification of dyes and lake pigments (Aceto, Agostino, Marcello, & Delaney, 2014). All the spectra obtained from these six miniatures show *apparent absorbance* maxima at 520 nm and 550 nm (Figure 24). These spectral bands correspond to those obtained via the cochineal lake preparation and paint standards created for this project, as well as the kermes, Mexican cochineal, and Armenian cochineal standards analyzed by Aceto, et al (2014).

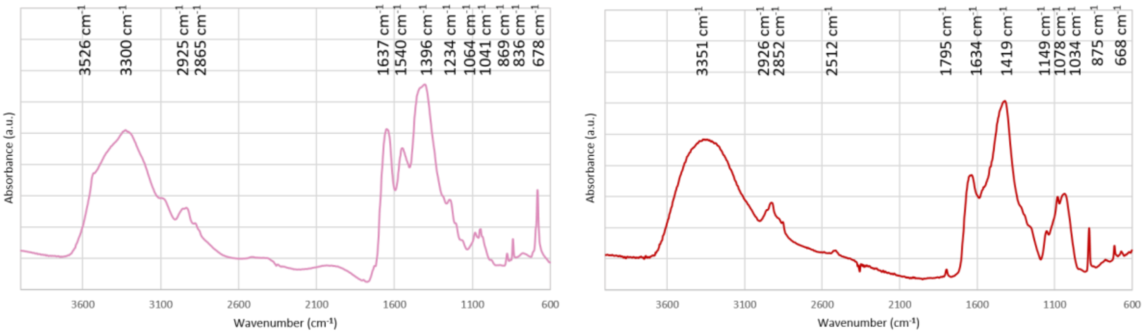


Figure 25: μ-FTIR analysis of red lake pigments. Left, taken from the pink tail of the figure on *f*.41v. Right, taken from the red background *f*.50v. (See Appendix II for exact sample locations.)

Three areas of suspected red lake pigments were sampled for invasive analysis. (Dark and light pink areas in *f*.41v and the red background of *f*.50r) The results from μ-Raman analysis were, as expected, not useful due to the overwhelming fluorescence of the lake pigments (Bisulca, Picollo, Bacci, & Kunzelman, 2008). μ-FTIR analysis of these samples yielded better results (Figure 25). When compared to reference library carminic acid spectra, there were clear similarities, specifically in the case of the sample from *f*.50r, which aligned

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[3] Three miniatures were studied on *f*.13v. The "-b" notation here indicates it is the second of three images on the page.

[4] The asterisk is used here to note an error in the page numbers written onto the top right corner of the manuscript pages. This page is unnumbered, but is found between *f*.39 and *f*.40.

well in the 950-1150 cm^{-1} region, as well as at 2852 cm^{-1} and 2927 cm^{-1}. The broad absorption bands around 3400 cm^{-1} is likely due to the presence of amorphous $Al(OH)_3$ due to an aluminum-containing substrate (Clementi, et al., 2008). The EDS results for these samples indicate that the light pink was likely mixed with lead white, (Lead accounting for 58% of the material by weight.) The results from *f*.50r also show the presence of S, P, Si, Ca, K, Cl, Mg which are all indicative of dyestuff trace elements (Kirby, Spring, & Higgitt, 2005). These elements are not found in the pink areas of *f*.41v, however these elements are likely missing due to being mixed with a large amount of lead white and are in so small a percentage as to not register.

3.2.2.1.2 INORGANIC PIGMENTS

Two types of inorganic red pigments were identified: minium and vermilion. Minium, or red lead (Pb_3O_4) was found in the miniature on *f*.41v and that of *f*.48v. These areas were confirmed as minium due to the high lead peaks found via XRF analysis, as well as FORS spectra showing an inflection point at 565 nm. (Aceto, Agostino, Marcello, & Delaney, 2014) The brighter orange-red color of the area analyzed on *f*.41v suggests that it may have been mixed with lead white.

Vermilion (HgS) was found in the miniatures *f*.15v and *f*.13r-a. The FORS spectra show a standard inflection point of 600 nm. The XRF results show Hg as expected, but the S $K\alpha$ peaks are unidentifiable due to overlap with the $M\alpha$ peaks of Pb. The Pb peaks here may indicate the presence of lead white. Red text analyzed on *f*.13r also proved, via FORS and XRF, to be composed of vermilion.

3.2.2.2 YELLOW

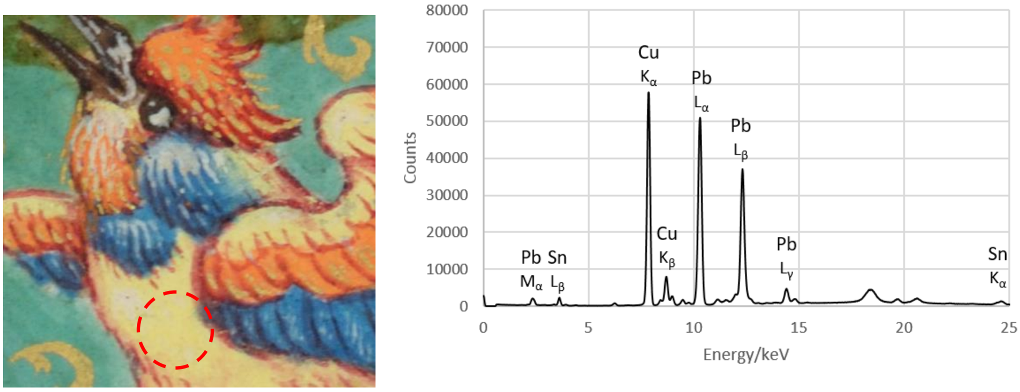

Figure 26: XRF spectra of yellow pigment used on the chest of the bird on *f*.13v-c
Images © BPE and HERCULES Lab

Two types of yellow paints were identified within the selected miniatures. The first type was found on the birds in miniatures *f*.13r-b[5] and *f*.13v-c. These areas were clearly identified as lead tin yellow using XRF (Figure 26). These areas were not analyzed with FORS, as the area was too small to get an accurate measurement. While the XRF spectra also contains Cu, this is likely due to the large spot size of the XRF and the close proximity of both Cu-based blues and greens. The presence of Sn and Pb in combination with its bright, clear yellow color left little doubt as to the nature of the pigment. In the interest of keeping destructive methods to a minimum, no further samples were taken from these areas.

The second type of yellow paint was identified as a mix of a yellow lake and ochre. This mixture was found both in the background of the miniature of *f*.9v as well as underneath the gilding on *f*.37v. The µ-Raman results were obscured heavily by fluorescence, indicating the presence of organic materials. EDS results show the presence of Fe, Si, and Al supporting the presence of a clay and iron oxide mixture in the form of an ochre. The presence of Na is

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[5] Again, referring to the second miniature analyzed on *f*.13r.

likely due to the natural elements found in the dyestuff (Kirby, van Bommel, & Verhecken, 2014).

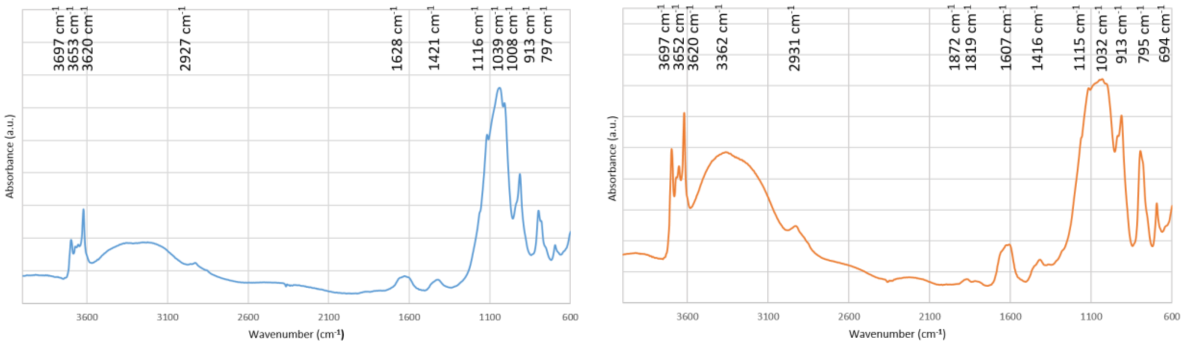

Figure 27: FTIR spectra of yellow pigment. Left, sample taken from yellow background of *f*.9v. Right, sample taken from pigment ground found underneath the gilded background of *f*.37v. (See Appendix II for exact sample locations.)

FTIR spectra for both areas of yellow show typical peaks for kaolinite at 3697, 3669, and 3652 cm^{-1}, due to the stretching of O-H bonds within the outer hydroxyl ions, as well as the inner hydroxyl ions represented at 3620 cm^{-1} (Bikiaris, et al., 1999; Stuart, 2004). These samples also have broad bands at 3400 cm^{-1}, similar to the red lake samples indicating an aluminum-containing substrate (Figure 27).

As has been extensively explored, FORS results are notoriously difficult to identify in the case of mixtures (Aceto, Agostino, Marcello, & Delaney, 2014). Samples of weld and buckthorn lakes were prepared, as explained above, and were analyzed alone as well as mixed with yellow ochre. However, neither could be sufficiently matched to the sample spectra and the yellow lake remains unidentified.

3.2.2.3 BLUE

A copper based blue, likely azurite, appears to be the constant variety of blue pigment found throughout the manuscript. Each area analyzed presented a similar FORS spectra, though there were slight variations between all of them, with *reflectance maxima* ranging from 458-

475 nm. Two azurite paint standards were analyzed, one with a dark hue and the other lighter. The difference between these is similar to those observed in the manuscript, with *reflectance maxima* at 445 nm and 472 nm, respectively. It is possible that this range is due to variations in how coarsely the pigment was ground. In the case of the dark blue area on *f*.33r, this shift is likely due an unidentified dark paint layer creating the shadow.

Figure 28: Differences in blue hue. Right, *f*.7r. *Left*, *f*.33v
Images © BPE and HERCULES Lab

These variations may also be due to the use of pigment mixtures, as they are not all the same hue (Figure 28), however there are no other aspects to their FORS spectra (other than the shift discussed above) that could definitively indicate an additional pigment, such as the characteristic sigmoid inflection point associated with indigo or woad (Aceto, Agostino, Marcello, & Delaney, 2014). Further investigation is necessary to determine the exact nature of these areas.

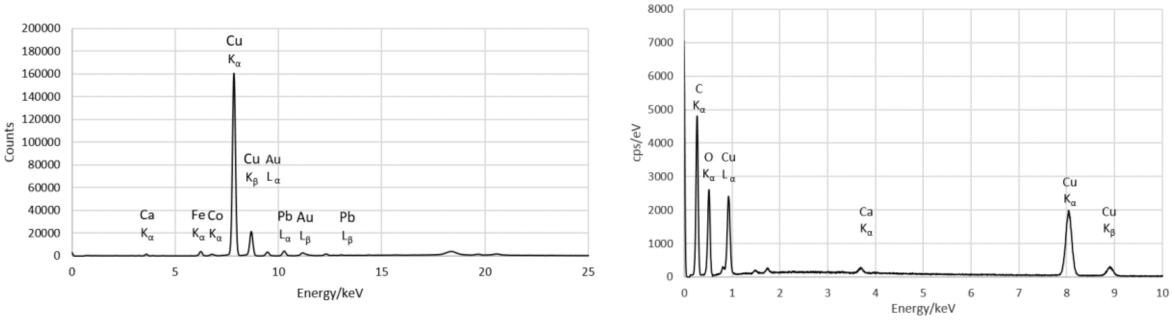

Figure 29: *f*.7r - Blue background. Left, XRF spectra. Right, EDS spectra.

The XRF analysis of the miniature on *f*.7r showed the presence of Co and K (though K is present in all analyses, as it is associated with the parchment itself) (Figure 29). This suggested the presence of smalt. Paint samples prepared with a 10%wt mixture of smalt in azurite gave FORS spectra that are similar to that obtained from the manuscript, however they are also very similar to the spectra of azurite alone, the characteristic spectral features of smalt being very weakly apparent. While SEM-EDS results showed a very small amount of Si, there was no evidence of Co nor K (Figure 29). It is possible that the Co is due to the use of smalt in small areas of blue in the opposing miniature on *f*.7v, though this does not explain the Si found in the sample.

The chemical composition of smalt is variable with approximately 65-72 wt % SiO_2, 10-21%wt K_2O, 2-18 wt % CoO, and possible small amounts of As_2O_3 and various impurities such as Al_2O_3 (Mühlthaler & Thissen, 1993). The fading of smalt was a known issue historically and is due to potassium being leached away from the cobalt into the binder or surrounding glass particles, not due to the loss of cobalt (Boon, Keune, van der Weerd, Geldof, & van Asperen de Boer, 2001). While 0.05wt% Si was detected by EDS, this is below the detection limit for the equipment and cannot be used to determine the presence of Si. If there is smalt present here, it may vary throughout the paint layer, being more concentrated in the site of the XRF analysis. It is possible that the Co found via XRF exists instead on the back side of the page. Unfortunately, further investigation into the opposing miniature could not be done due to time and malfunctioning equipment.

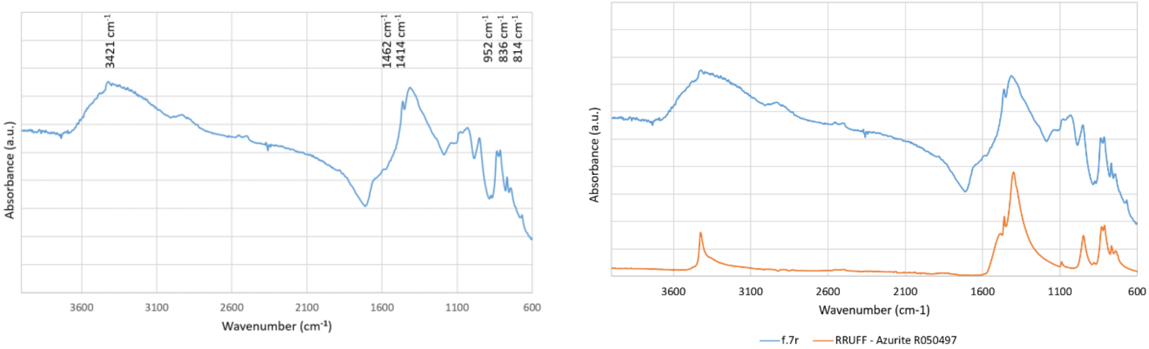

Figure 30 Left, FTIR Spectra of *f*.7r blue pigment. Right, comparison with and azurite standard[6]

Evidence of azurite is seen in the Raman spectra, with the characteristic strong band at 403cm^{-1}. The FTIR spectra was negatively affected by the small sample size and thin dispersion of the particles, however it clearly shows the presence of azurite (Figure 30). The bands at 1414, 836, and 814 cm^{-1} are due to the absorption of $-CO_3$, while the bands at 952 and 3421 cm^{-1} are due to the out-of-plane bending of the hydroxyl group (Gettens & Fitzhugh, Azurite and Blue Verditer, 1993). The bands between 1135-1032 cm^{-1} may be due to asymmetric stretching of Si-O-Si (Derrick, Stulik, & Landry, 1999).

3.2.2.4 GREEN

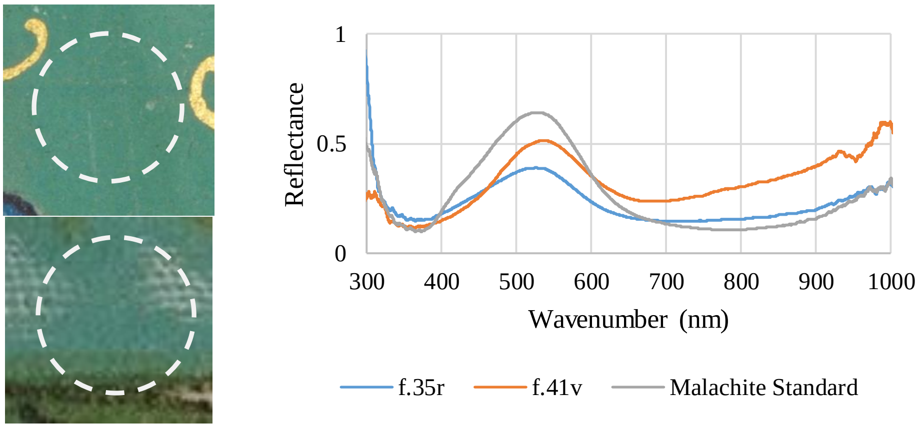

Figure 31: FORS Spectra of *f*.35r, 41v, and a malachite standard.
Top thumbnail: *f*.35r. Bottom: *f*.41v.

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[6] http://rruff.info/Azurite/R050497

Six green areas were analyzed by XRF, two of which had large enough areas to accommodate FORS analysis as well. All of the XRF results (complicated, as stated above, with information from the inks on the other side of the page) show the presence of a copper-based pigment. The FORS analysis on *f*.35r and *f*.41v show the typical spectra of malachite, with *reflectance maxima* at around 530 nm, the slight red-shift seen in the *f*.41v spectra is likely a result of analyzing over a partial area of shadow (Figure 31). The XRF spectra of the miniatures on *f*.14v and *f*.39*r show a mixture of some copper pigment (it is unknown if it is a green or a blue) with lead tin yellow. It is possible that some form of organic blue such as indigo or woad was used in this mixture and the Cu is originating from the pure blue around the spot analyzed or from ink on the back side of *f*.39*r.

3.2.2.5 PURPLE

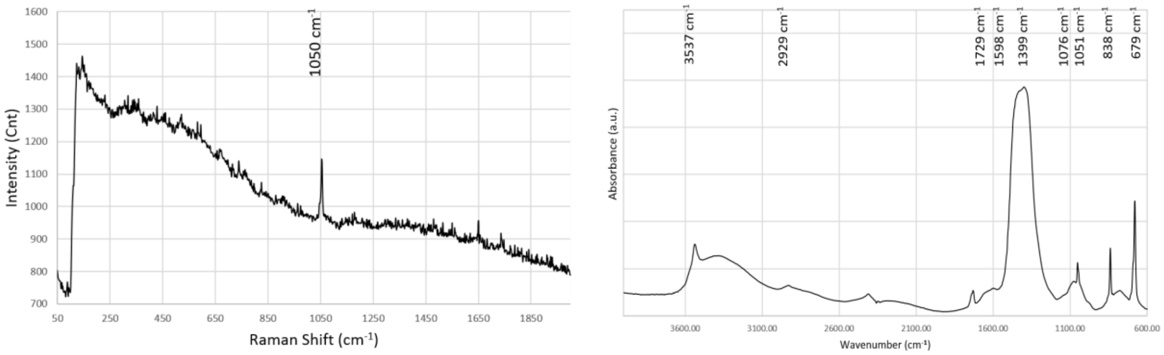


Figure 32: µ-Raman and µ-FTIR spectra of the micro-sample from the purple border of *f*.9v.

Two types of purple paint mixtures were analyzed within the manuscript. One found on *f*.9v and another on *f*.53v. As mentioned previously, *f*.9v was suspected of being painted at a different time or, at the very least, by a different artist. Further analysis shows that the two shades of purple are created via different pigment mixtures. The border of *f*.9v is composed of a Cu-based pigment, lead white, and an unidentified organic pigment. Due to the presence of an organic pigment, only lead white is visible in the Raman spectra, with a clear band at

1050cm^{-1} (Figure 32). The FTIR spectra also shows the presence of lead white ($PbCO_3 \cdot Pb(OH)_2$) with bands at 1399, 1051, and 679 cm^{-1} corresponding to carbonate stretching vibrations, while the sharp band at 3537cm^{-1} representing hydroxyl stretching (Gettens, Kühn, & Chase, 1993). The presence of azurite is masked by the lead white bands in both the Raman and FTIR spectra, and EDS confirms that the presence of Cu is very low at 1.11wt% in comparison to Pb at 70.12wt% (Figure 33).

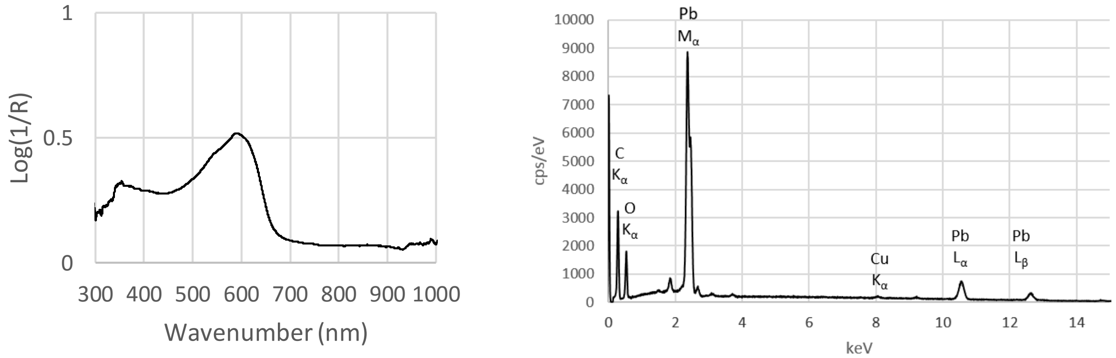


Figure 33: *f*.9v - Purple border. Left, FORS spectra. Right, EDS spectra.

The organic component of this mixture is unknown, however the FORS spectra shows absorption peaks at approximately 545 and 590 cm^{-1}, which may correspond to orchil or elderberry dyes, however more investigation is necessary to identify further (Figure 33) (Aceto, et al., 2015; Bicchieri, 2014).

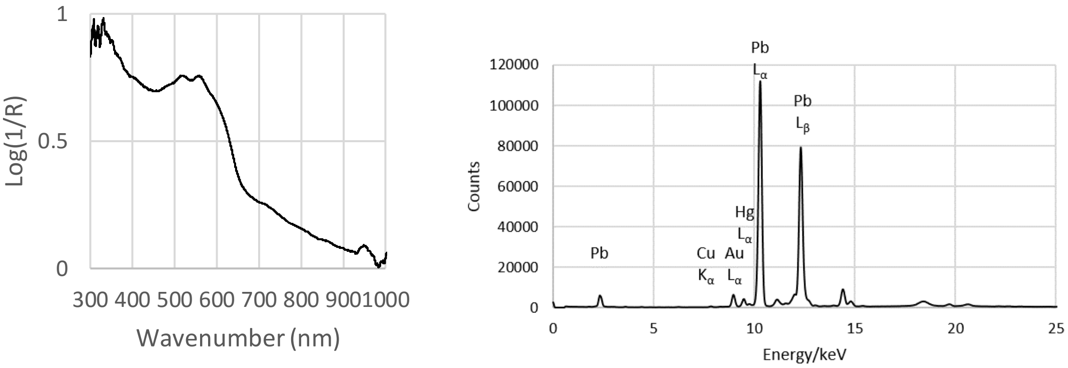


Figure 34: *f*.53v - Purple background. Left, FORS spectra. Right, XRF spectra.

The purple of *f*.53v was not micro-sampled. *In situ* analyses show a mixture of a Pb and Cu-based pigments and an insect-based lake. The site of the XRF analysis was not over any black ink on the opposite side of the page, so the small Cu peak can be considered to come from a small amount of blue pigment, possibly azurite (Figure 34). As with the previous purple area, this appears to be a combination of a large amount of lead white and azurite, this time utilizing the cochineal or kermes lake found throughout the rest of the manuscript.

3.2.2.6 INKS

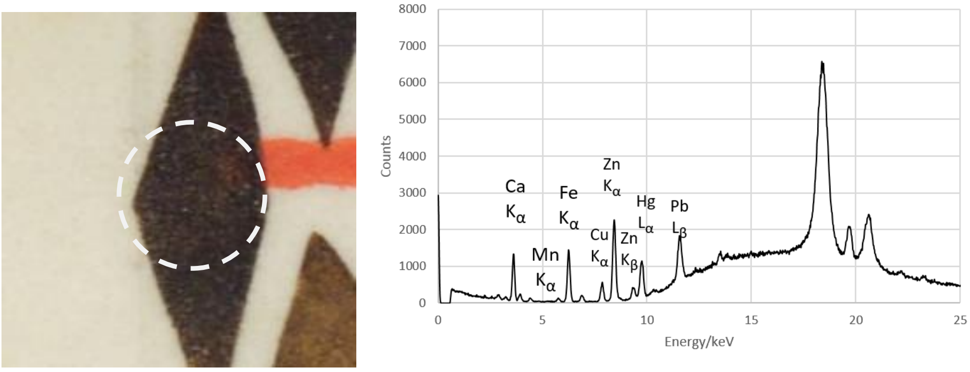


Figure 35: *f*.53v - Photographic image of black ink. Right, corresponding XRF spectra.

As mentioned previously, nearly all XRF results throughout the manuscript showed Hg, Fe, and Zn peaks which did not make sense when compared with FORS spectra and other methods. Upon analyzing the inks alone and superimposing images of each miniature with its corresponding back side, it became clear that these elements were originating from the inks and potentially from ruling lines laid down using a metal stylus. Even XRF analysis of the inks themselves are not immune to these contaminations, as seen in the spectra of black ink on *f*.53v (Figure 35). While Hg is clearly seen here, corresponding to red staff lines from the opposite side, the rest of the elements are what is expected of iron gall ink: Fe, Cu, Mn, and Zn, the last three elements often found as impurities within green vitriol (Manso, et al., 2015). There is a large amount of Zn present in the ink, also seen in black ink analyzed on *f*.37v, which surpasses the amount of Fe.

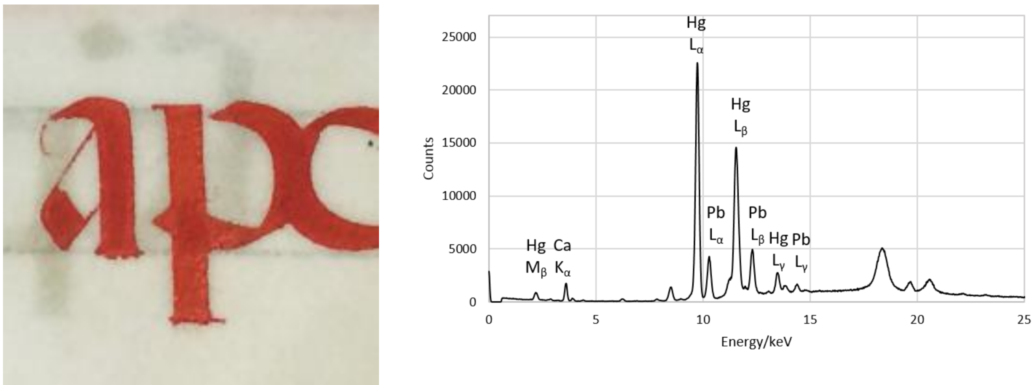
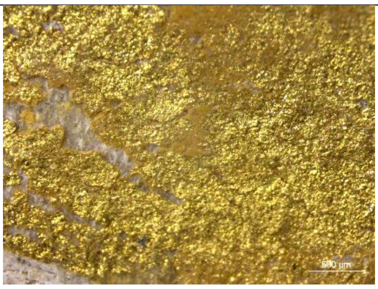


Figure 36: *f*.13r - Photographic image of red ink. Right, corresponding XRF spectra.

The red ink is used throughout the manuscript for rubrics and the lines of the staves. The XRF spectra clearly show a large presence of Hg, indicating the presence of vermilion (Figure 36). There is a small amount of Pb (obscuring, as described previously, any S Kα peaks), but it is unclear as to whether this is due to a mixture with red lead, the use of lead white as an extender, or information gained from the other side of the page.

3.2.3 GILDING

Table 5: Microscopic photos of gilding on *f*.37v and *f*.50r and gold alloy composition

f.37v 	Au : Ag : Cu 97:1:2, % wt
f.50r 	Center area: Au : Cu 97:3 % wt Outer area: Au : Cu 96:4, % wt

Three areas of gilding within two miniatures were analyzed with SEM-EDS: both the light and dark variations of gold used in the modeling of the letter on *f*.50r, as well as the gold background of *f*.37v. As anticipated, the composition of gold used in these miniatures is different. Neither utilize pure gold. Both miniatures use a combination of Au and Cu, with *f*.37v containing the addition of Ag (Table 5).

These mixtures could have been created via the fire amalgam technique, spoken of frequently in the treatises, in which the base metals were heated in mercury. The heating removes the mercury and the resulting ground metal could be mixed with glair or arabic gum and used as a pigment, similar to what is seen in this manuscript (Clarke M. , 2011; Thompson, 1936).

3.2.4 BINDERS AND EXTENDERS

The binders used within the manuscript are difficult to identify due to the complex FTIR spectra resulting from pigment mixtures. Of the micro-samples analyzed, it appears that a proteinaceous binder was used throughout the manuscript. The main identifying spectral features of proteinaceous binders (such as glair or parchment glue) are that of amide I (~1650cm^{-1}, C=O stretching), amide II (~1550cm^{-1}, C-N-H bending), amide III (~1450cm^{-1}, C-H bending), and N-H stretching circa 3400-3000cm^{-1} (Derrick, Stulik, & Landry, 1999). Evidence of these bands occur in *f*.7r exhibiting a wide shoulder extending over 1650 and 1545 and a wide, low peak around 3400. Both *f*.9v and *f*.37v have similar spectra, with two peaks hidden around 1600cm^{-1}, and possibly one below 3000cm^{-1}. The micro-sample from *f*.41v shows a broadening of the shoulder around 1700cm^{-1} indicating amide I.

Due to the possibility of small amounts of parchment contaminating the micro-samples, *in situ* FTIR analysis was done on lake pigment recreations prepared with arabic gum, both to see if the mixtures matched the any unidentified pigments and to determine if the parchment ground would be seen in the resulting spectra. The polyamide pattern is absent from these samples, supporting the presence of a proteinaceous binder in the manuscript micro-samples.

Evidence of extenders is primarily seen in the EDS results and includes chalk ($CaCO_3$), lead white, and kaolinite (likely in the form of an ochre).

Table 6: Compiled results

Pigment/Mixture	Folia	Binder	Extender	Analytical Technique
Scale Insect (Kermes or Cochineal)	13v-b, 35r, 39*r, 41r, 42v, 50r	Protein	Chalk	FORS, XRF, µ-FTIR, µ-Raman, SEM-EDS
Vermilion (HgS)	15v, 13r-a, red text of 13r	-	-	FORS, XRF
Minium (Pb_3O_4)	41v, 48v	-	-	FORS, XRF
Unidentified Yellow Lake and Yellow Ochre	9v, 37v	Protein	Kaolinite	FORS, XRF, µ-FTIR, µ-Raman, SEM-EDS
Lead Tin Yellow	13r-b, 13v-c	-	-	XRF
Malachite	35r, 41v	-	-	FORS, XRF
Lead Tin Yellow and Cu-based pigment or unknown organic	14v, 39*r	-	-	XRF
Azurite	7r, 14v, 31r, 33r, 41v	Protein	Chalk	FORS, XRF, µ-FTIR, µ-Raman, SEM-EDS
Azurite and unknown organic, possibly orchil or elderberry	9v	Protein	Lead White	FORS, XRF, µ-FTIR, µ-Raman, SEM-EDS
Azurite, Kermes/Cochineal	53v	-	Lead White	FORS, XRF
Au + Cu 97:3 % wt	50r	-	Chalk	XRF, SEM-EDS
Au + Cu 96:4, % wt	50r	-	Chalk	XRF, SEM-EDS
Au + Ag + Cu 97:1:2, % wt	37v	-	-	XRF, SEM-EDS
Iron Gall Ink (Fe, Cu, Zn, Mn)	37v, 53v	-	-	XRF

4. CONCLUSIONS

By utilizing many complementary analytical techniques, this project was successful in gaining a greater understanding of the palette and painting techniques employed in this manuscript (Table 6). The use of fast, *in situ* techniques such as FORS allowed for, if not the exact identification of every pigment, the ability to document a far larger amount of the book than could be achieved with more invasive techniques, especially due to the physical limitations of the manuscript due to its large size.

The pigments identified correspond well to the historical documentation, such as the use of azurite over lazurite and mixing lead-tin yellow to create greens. The extensive use of insect-based lake pigments is supported by almost every analytical method used here. Determining whether or not this is kermes or a variety of cochineal would be of interest to art historians, as the presence of Mexican cochineal can support a relative production date. While the source of this lake cannot be confirmed based on current results, it can be determined by identifying the percentage of kermesic to carminic acid via HPLC (de Graaff, Roelofs, & van Bommel, 2004). This was not done during this project as the instrument was broken, however a micro-sample has been set aside and will be tested in the near future.

While the FORS spectra interpretation of paint mixtures continues to be difficult and few were definitively identified, the ability to experiment and create paint references allowed for certain mixtures to at least be partially ruled out. The creation of hypothetical mixtures used within the manuscript was most successful when built off of micro-sampling results. While destructive methods are not ideal, without them the results would have been completely misleading. The size of the sample area of the XRF instrument is simply too large to be very accurate with such small, detailed paintings and utilizing a µ-XRF instrument would likely have been more successful. The interference of information on the back side of the parchment was also completely unexpected. Further experimentation was planned to learn more about this and how the effect might be diminished, however this was not possible due to equipment scheduling and the instrument needing repair.

Overall, this project has not only gained more information about this one object, but laid the groundwork for future comparative studies to learn more about manuscript production within 16th century Portugal, potentially gaining a better understanding of the provenance of this and other unidentified manuscripts. The lake pigments and paint samples prepared can be used as references in subsequent investigations. Ideally, projects such as this will continue to add more paint mixtures, creating a larger library to draw from in the future.

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APPENDIX I: LAKE PIGMENTS AND PAINT SAMPLES

I.1 FULL MADDER LAKE RECIPE

The following is the full recipe for Madder Lake #1 in its original format. The lake pigment recipe was originally prepared for the CHARISMA Project workshop “Back to the Roots” hosted by the Doerner Institut in 2011. The website that this recipe was sourced from is no longer online, therefore a current reference cannot be given. Please see Materials and Methods Section 2.1.3.1 for specific amounts and ingredients used in this project.

MADDER DYE:

“Semelwater
The bath was prepared as follows:
Add 2 kg of bran of wheat to 45 l of water, bring to the boil, turn off heat, add 30 l of water and cover vat. Stir every hour (7x) during first day, after 6 days take out 40 l for recipe Red / S1, pH 4.87, add 40 l of hot water, stir and leave for another 24 hours, use 70 l for recipe Red / W1, pH 4.35.

Red / W1
The baths were prepared as follows:
6 wool hanks (1000 g)
70 l semelwater
150 g alum
600 g madder
50 g K_2CO_3

Mordanting:
To 50 l of semelwater, pH 4.35, add 150 g alum, dissolve, pH 3.17, immerse wool, bring to the boil and boil for 2 hours, drain, do not wring.

Dyeing:
To 20 l semelwater, pH 4.35, add 30 l of water, add madder, stir and bring up to 40°C, pH 5, immerse wool, raise temperature to 90°C and leave f or 3 hours, drain, rinse, wring and leave 3 hanks to dry.
Lye treatment:
In 50 l of water, pH 7.4, dissolve K_2CO_3, pH 10.95, 20°C, immerse 3 hanks and leave for 30 min, rinse.” (Hacke, 2006)

MADDER LAKE:

“Madder, Rubia tinctorum L., powdered root used for the MODHT European project, bought from Verfmolen De Kat, Kalverringdijk, 29, 1509 BT Zaandam, was used for Recipe 1. Alum-mordanted wool dyed with the same madder following a recipe from Tbouck van wondre, Brussels 1513, as part of the MODHT (Monitoring of Damage to Historic Tapestries) project

Chemicals:
Potash alum, aluminium potassium sulfate dodecahydrate, $KAl(SO_4)_2\cdot 12H_2O$, laboratory grade reagent, Fisher Scientific UK Ltd, Loughborough, LE11 5RG, UK. Code A/2400/60; batch 0272837, CAS 7784-24-9, packed 23.06.2003.
Sodium carbonate, Na_2CO_3, anhydrous, BDH laboratory reagent, BDH (British Drug Houses) Laboratory Division, Poole, Dorset, UK, 324010 (old sample, in good condition). Potassium carbonate, K_2CO_3, 99+% ACS reagent, Sigma-Aldrich Co. Ltd, The Old Brickyard, New Road, Gillingham, Dorset, SP8 4XT, UK, 20,961-9, lot 52164-224, CAS 584-08-7.
Water freshly distilled in the laboratory used throughout.
Note: If filtration while the solution is still hot is recommended, filtration is slow and vacuum filtration is unavailable, it is suggested that a parallel series of filtrations is set up, with filter papers of a suitable grade, fluted, being regularly replaced; all the filtrates can then be recombined.

RECIPE 2 – FIFTEENTH-CENTURY TYPE MADDER LAKE This recipe also gives a pigment with a high sulphur content in the substrate, in this case associated with the presence of wool protein. Similar pigments have been identified in 15th- and 16th-century lake pigments in samples of oil paint, from northern Europe in particular. The recipe consists of denaturing wool shearings in alkali to form a jelly-like material that is ground with a little alum to give a pigment, here numbered 2ii. During this process, the alkali becomes highly coloured by dissolved dyestuff (with wool protein also present in the solution). In order not to waste this dye – only a limited amount of the original dyed wool was available – and to give a madder pigment with different characteristics that might also be identified in pigments from painted artefacts, a pigment, numbered 2i, was also made from this solution, although this is not part of the original recipe. The procedure requires careful monitoring. Recipe derived from E.E. Ploss, Ein Buch von alten Farben: Technologie der Textilfarben im Mittelalter mit einem Ausblick auf die festen Farben, Heidelberg and Berlin 1962, the Nuremburg Kunstbuch (15th century) pp. 113–14. 40 g madder-dyed wool (MODHT recipe Red/W1) were clipped as finely as possible using sharp scissors to give clippings (‘shearings’) about 1–2 mm long. This stage is important: the smaller the pieces (fluff, rather than fibres), the better. A solution of 41.4 g potassium carbonate (K2CO3) in 1 l water (a 0.3 M solution) was brought to the boil and its strength tested with a feather in the manner given in the recipe: if the vane of the feather when dipped into the solution could easily be stripped from the central quill, the solution was strong enough. The wool was then added to the solution and left to boil for 1 hour in the fume cupboard (unpleasant smell of sulphur). The red wool mass, largely reduced to a jelly by this treatment, was filtered using a nylon sieve and fine nylon net and the dark red filtrate was used for the additional pigment, lake 2i.

Lake 2i (additional pigment): Potash alum ($KAl(SO_4)_2\cdot 12H_2O$) crystals were added to the dark red filtrate obtained as described above until the pH appeared to be 7 (50 g potash alum were needed).

The pale red precipitate was then left to settle till the following day. Dissolution of the alum was not, however, complete (some rose to the surface and was skimmed off). The next day, as the pH was found still to be alkaline, the mixture was heated and more potash alum in solution (30g potash alum in 150 ml water) was added until the pH was neutral. The pale red-orange pigment was left to settle until the following day. (Note: Although it is common in medieval recipes for the alum to be added in crystalline form, it is easier and more efficient in practice to dissolve it in distilled water and add it as a solution.)

The lake was filtered using a Buchner funnel with a Grade 113 Whatman filter paper, a side-arm filter flask and a vacuum pump. The precipitate was not allowed to go to dryness and was washed thoroughly with distilled water until the filtrate was completely colourless. The precipitate was then taken to dryness, transferred to a dessicator and stored over silica gel until thoroughly dried. The dry pigment was ground using a mortar and pestle.

Lake 2ii (intended pigment): The red mass obtained as described above was transferred from the sieve to a shallow porcelain evaporating dish and heated in a solution of c. 14 g K_2CO_3 in 200 ml water (about 0.5 M), testing the mass with a glass rod until it appeared that no wool fibres were left and the material had been converted to a jelly-like consistency. The jelly-like solid was then filtered using the sieve and nylon net as before and washed with distilled water. It was then laid on a ground glass slab and ground with 10g potash alum (a quarter of the mass of the original wool; during the mixing water was released). The product was then put into 1 l distilled water, which was brought to the boil. It tended to rise to the surface as a coherent mass. After a few minutes boiling it was easily filtered using a Buchner funnel with a Grade 113 Whatman filterpaper, a side-arm filter flask and a vacuum pump. It was transferred to a dessicator and stored over silica gel until thoroughly dried. After drying the red lake was ground using a mortar and pestle.”

I.2 COLORIMETRIC ANALYSIS OF PREPARED PAINT SAMPLES

Table AP I.1: Colorimetric data of prepared paint samples

	Average CIE L*a*b*											
Pigment(s)	**Parchment Glue**			**Egg White**			**Egg Yolk**			**Arabic Gum**		
Brazilwood Lake	30.40 ±0.29	27.34 ±0.87	-4.18 ±0.29	30.82 ±1.42	25.26 ±0.36	1.30 ±0.57	27.57 ±0.44	19.41 ±1.7	4.47 ±0.50	28.41 ±0.64	25.79 ±0.45	-1.32 ±0.33
Cochineal Lake #1	46.24 ±1.78	28.86 ±0.77	-11.42 ±1.73	43.26 ±1.93	27.63 ±0.93	-9.21 ±0.50	33.72 ±0.93	25.21 ±0.80	-1.28 ±0.42	40.26 ±1.30	30.08 ±1.04	-9.50 ±0.52
90:10%wt, Vermilion : Red Ochre	39.70 ±0.14	27.70 ±0.08	16.04 ±0.11	38.88 ±0.63	24.76 ±0.75	13.12 ±0.56	41.05 ±1.40	31.40 ±2.31	20.26 ±0.42	40.48 ±0.45	27.71 ±0.88	16.14 ±0.89
90:10%wt, Vermilion : Minium	45.32 ±0.64	39.85 ±0.91	22.43 ±0.81	44.33 ±1.06	39.06 ±0.97	21.71 ±0.69	43.00 ±0.97	42.42 ±0.45	27.33 ±0.05	43.56 ±0.40	37.13 ±0.73	20.55 ±0.84
90:10%wt, Vermilion : $CaCO_3$	43.85 ±0.77	38.47 ±0.51	21.03 ±0.37	42.23 ±0.70	37.64 ±1.11	20.66 ±0.21	45.04 ±1.32	40.64 ±2.29	24.96 ±2.48	44.19 ±0.55	37.33 ±0.35	20.05 ±0.65
90:10%wt, Vermilion : $CaSO_4$	45.07 ±0.22	37.86 ±1.93	21.77 ±1.34	42.10 ±0.48	39.29 ±0.80	22.66 ±1.24	41.46 ±0.88	42.06 ±1.13	26.25 ±1.51	43.22 ±0.60	37.83 ±0.84	20.70 ±0.65
90:10%wt, Vermilion : Lead White	44.18 ±0.55	37.40 ±1.13	20.64 ±0.76	41.75 ±0.82	37.76 ±1.40	23.16 ±0.77	43.26 ±1.14	40.43 ±0.48	24.90 ±0.88	44.10 ±0.51	36.85 ±1.38	20.56 ±1.22
Madder Lake[7]	49.01 ±1.88	30.99 ±0.76	4.35 ±0.22	43.30 ±0.70	35.79 ±0.72	3.45 ±0.98	37.48 ±0.87	30.09 ±1.55	11.11 ±0.50	45.22 ±0.59	36.62 ±0.73	4.43 ±0.14
90:10%wt, Vermilion : Cochineal Lake #1	43.91 ±0.70	34.68 ±0.64	14.45 ±1.31	41.79 ±0.85	36.20 ±0.87	18.41 ±0.82	44.22 ±1.53	39.16 ±1.94	23.39 ±1.96	42.15 ±1.37	36.53 ±1.82	18.62 ±0.17
Yellow Ochre	56.92 ±0.63	21.66 ±0.18	44.43 ±0.29	52.76 ±0.40	18.31 ±0.25	37.59 ±0.33	57.85 ±0.88	20.32 ±0.06	46.92 ±0.45	56.51 ±0.68	19.76 ±1.12	39.70 ±1.54
Weld Lake	75.97 ±0.86	-4.36 ±0.03	37.68 ±0.48	74.08 ±1.07	-2.34 ±0.93	45.32 ±4.55	73.73 ±0.46	1.77 ±0.57	55.60 ±1.59	85.18 ±1.14	-5.01 ±0.06	33.81 ±0.49
90:10%wt, Weld Lake : Yellow Ochre	67.12 ±0.56	9.15 ±0.48	38.87 ±1.50	68.39 ±4.04	10.28 ±2.62	45.65 ±4.69	63.65 ±0.88	17.73 ±0.51	55.35 ±0.71	74.42 ±2.59	6.50 ±0.54	38.36 ±1.43
Buckthorn Lake	60.01 ±0.96	10.60 ±0.35	56.74 ±2.88	55.72 ±2.25	15.29 ±2.23	58.76 ±2.03	53.84 ±2.08	18.66 ±1.51	55.25 ±2.78	68.77 ±0.53	7.66 ±0.44	62.13 ±0.80
90:10%wt, Buckthorn Lake : Yellow Ochre	58.52 ±0.83	16.11 ±0.35	54.94 ±1.62	56.08 ±1.29	18.37 ±0.63	54.88 ±1.54	49.53 ±0.39	21.83 ±0.25	45.40 ±1.26	62.49 ±1.77	14.29 ±1.42	58.20 ±1.64
Cochineal Lake #2	48.00 ±0.49	30.60 ±1.25	-5.49 ±0.97	36.77 ±1.57	37.17 ±1.04	-4.77 ±1.54	36.18 ±1.21	35.06 ±1.19	4.02 ±0.27	41.85 ±1.87	38.54 ±0.32	-5.32 ±0.98
Cochineal Lake #3a	40.88 ±1.29	26.37 ±0.46	0.90 ±0.35	27.74 ±1.04	26.08 ±1.41	1.69 ±0.18	30.74 ±2.90	24.37 ±2.74	2.92 ±0.80	35.93 ±3.31	26.91 ±2.67	1.11 ±1.11
Cochineal Lake #3b	30.28 ±0.92	27.60 ±0.54	2.83 ±0.12	30.16 ±3.38	26.63 ±2.73	3.22 ±0.47	33.25 ±3.44	28.52 ±0.23	4.43 ±0.25	30.95 ±1.86	33.80 ±2.82	3.72 ±0.43
90:10%wt, Azurite : Lead White	69.27 ±0.61	-9.36 ±0.18	-9.08 ±0.61	67.98 ±1.67	-8.83 ±0.30	-8.23 ±0.75	54.31 ±1.59	-10.51 ±0.22	-9.31 ±0.66	55.28 ±1.73	-12.19 ±0.57	-11.68 ±2.11
90:10%wt, Azurite : Smalt	42.94 ±3.19	-8.08 ±3.20	-20.14 ±3.07	35.05 ±0.49	-7.79 ±0.94	-12.55 ±1.61	36.75 ±0.75	-10.65 ±1.16	-2.92 ±1.21	33.20 ±1.12	-6.00 ±0.57	-15.88 ±2.52
90:10%wt, Azurite : $CaCO_3$	43.87 ±0.88	-9.49 ±0.95	-16.17 ±1.80	39.87 ±0.47	-10.02 ±0.66	-10.17 ±1.24	39.30 ±1.8	-13.76 ±0.75	-2.51 ±0.33	39.97 ±1.39	-11.29 ±1.79	-11.40 ±1.89

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[7] Created by Ana Manhita, HERCULES Laboratory.

Table AP I.1 Continued: Colorimetric data of prepared paint samples

Madder Lake[8]	46.51 ±0.59	25.72 ±0.22	16.04 ±0.81	38.98 ±1.92	27.00 ±0.35	21.04 ±1.40	37.14 ±0.57	26.53 ±0.43	22.18 ±1.52	47.69 ±0.86	25.53 ±0.71	16.84 ±0.71
90:10%wt, Lake Cochineal #2 : CaCO$_3$	-	-	-	37.52 ±0.64	37.28 ±1.56	-9.35 ±1.72	-	-	-	44.55 ±1.42	35.30 ±0.68	-13.69 ±0.36
90:10%wt, Cochineal Lake#2 : CaSO$_4$	-	-	-	38.17 ±1.53	38.29 ±1.31	-7.93 ±1.81	-	-	-	45.11 ±0.61	34.78 ±1.01	-12.17 ±0.48

I.3: FORS SPECTRA OF PREPARED PAINTS TO BE USED AS REFERENCE MATERIALS

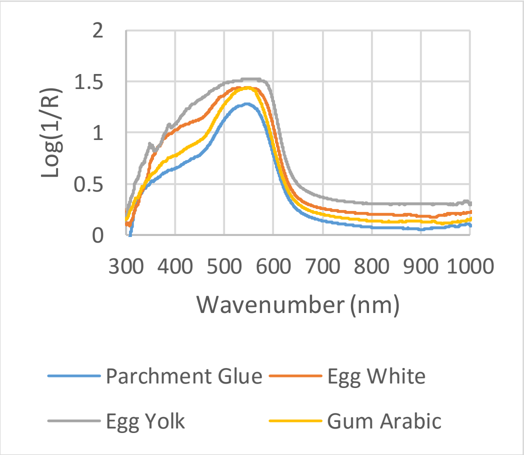

Figure AP I.1: FORS spectra of brazilwood lake

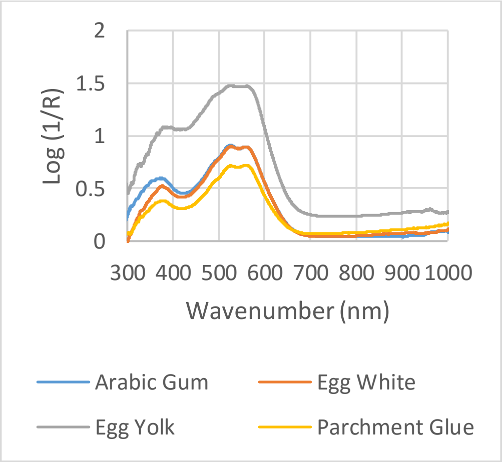

Figure AP I.2: FORS spectra of cochineal lake #1

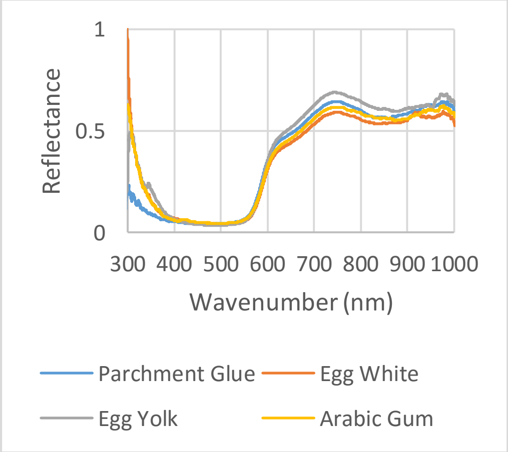

Figure AP I.3: FORS spectra of 90:10%wt, vermilion : red ochre

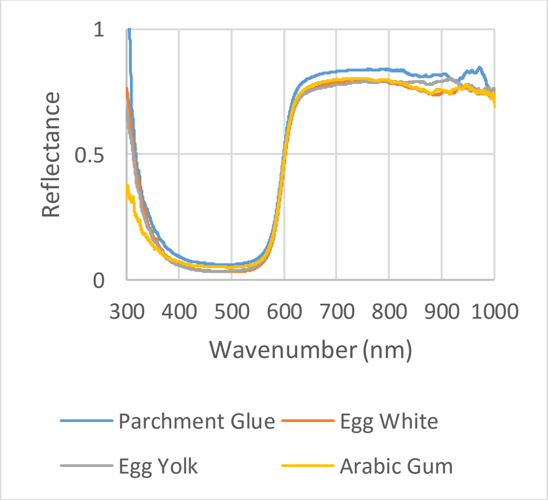

Figure AP I.3: FORS spectra of 90:10%wt, vermilion : minium

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[8] Created for this project. As stated in the text, this lake pigment was not successful, resulting in non-standard color and FORS spectra.

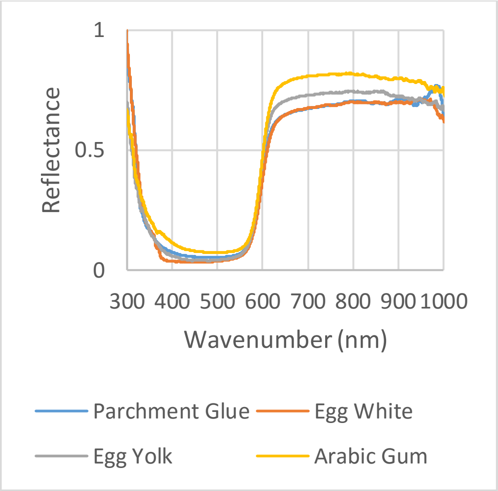

Figure AP I.4: FORS spectra of 90:10%wt, vermilion : $CaCO_3$

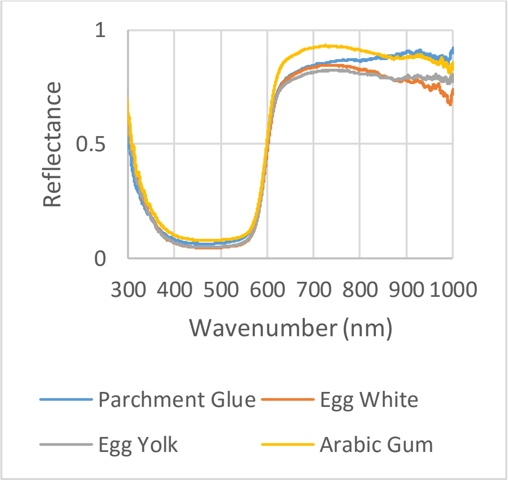

Figure AP I.5: FORS spectra of 90:10%wt, vermilion : $CaSO_4$

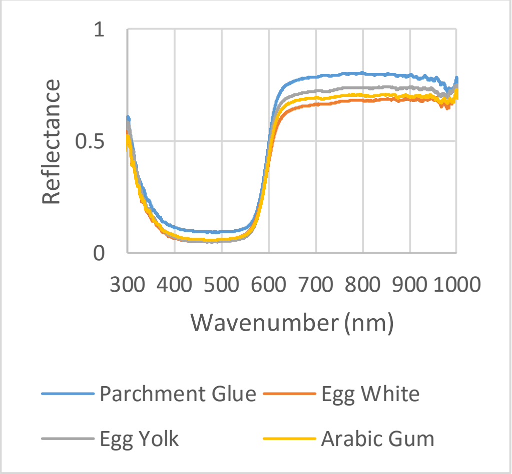

Figure AP I.6: FORS spectra of 90:10%wt, vermilion : lead white

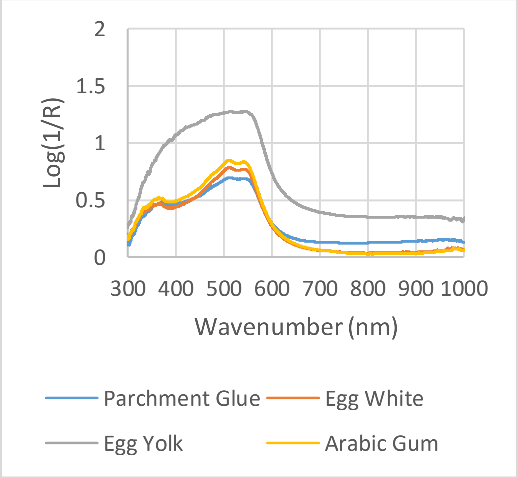

Figure AP I.7: FORS spectra of madder lake

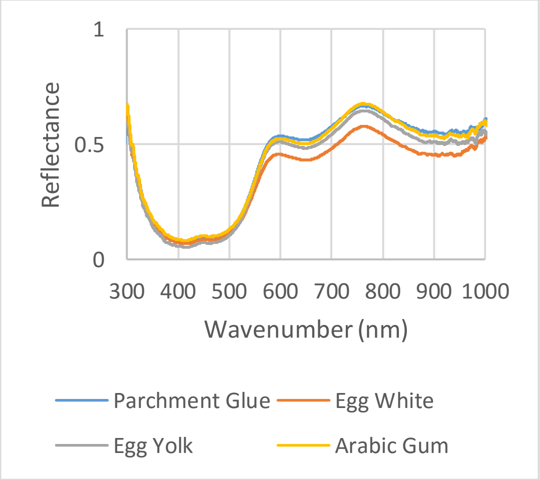

Figure AP I.8: FORS spectra of yellow ochre

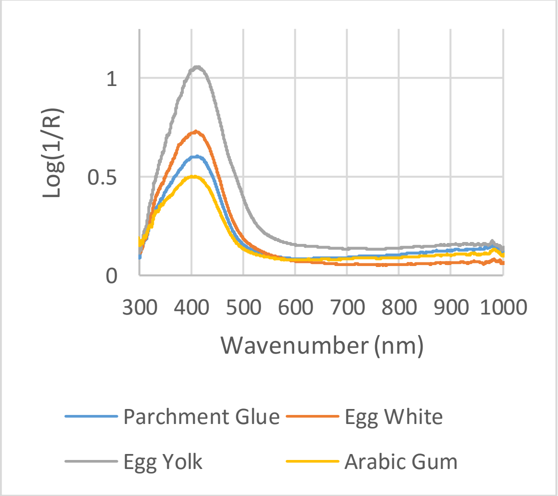

Figure AP I.9: FORS spectra of weld lake

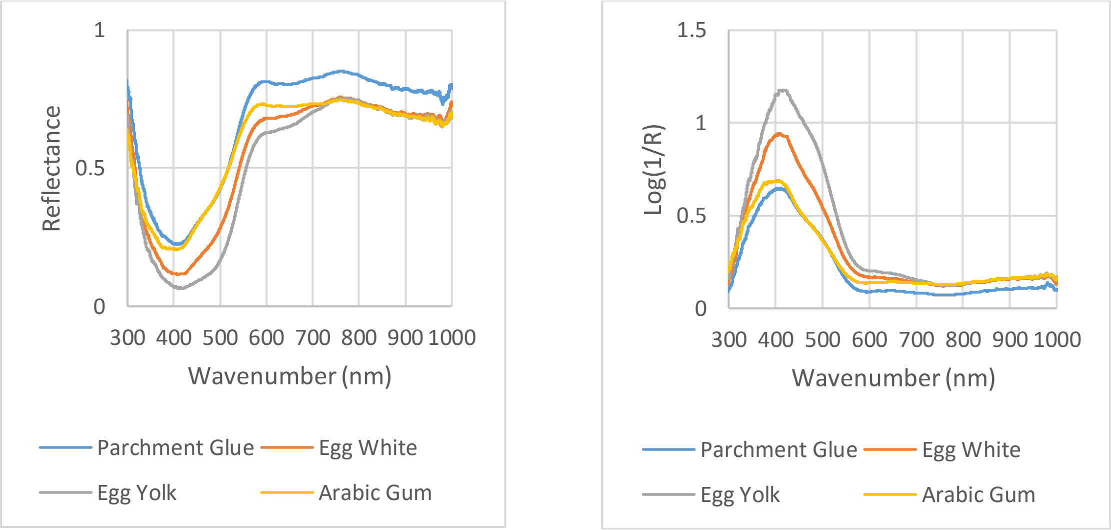

Figure AP I.10: FORS spectra of 90:10%wt, weld lake : yellow ochre. Left, reflectance. Right, apparent absorbance.

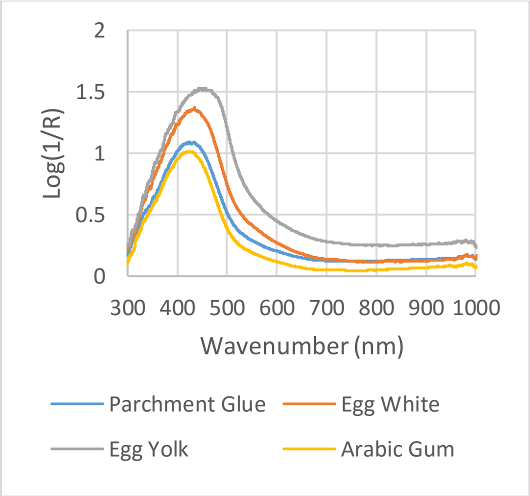

Figure AP I.11: FORS spectra of buckthorn lake

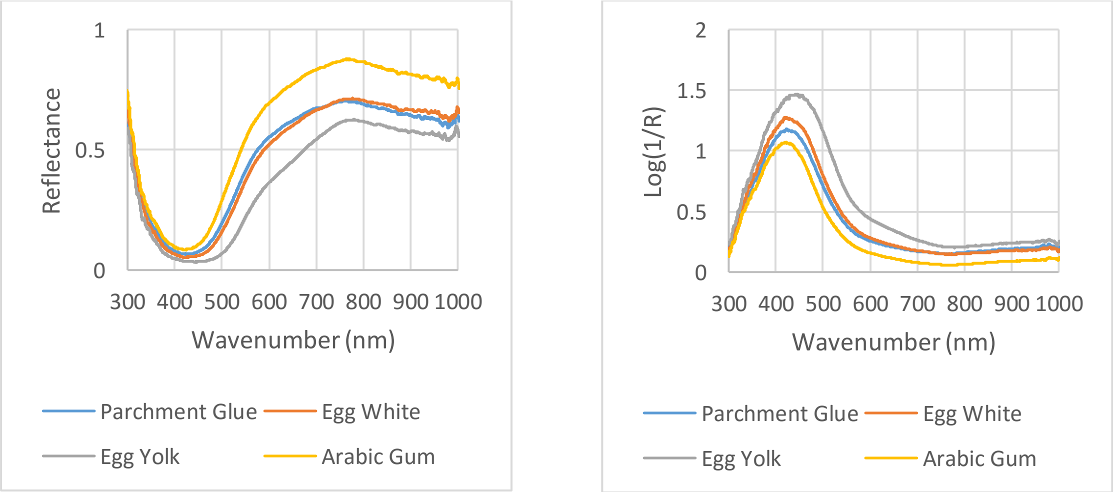

Figure AP I.12: FORS spectra of 90:10%wt, buckthorn lake : yellow ochre. Left, reflectance. Right, apparent absorbance.

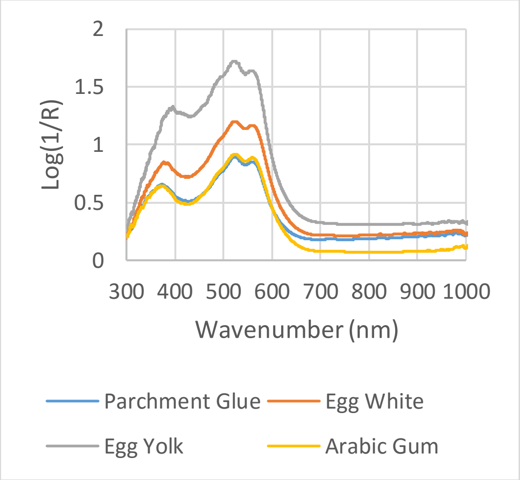

Figure AP I.13: FORS spectra of cochineal lake #2

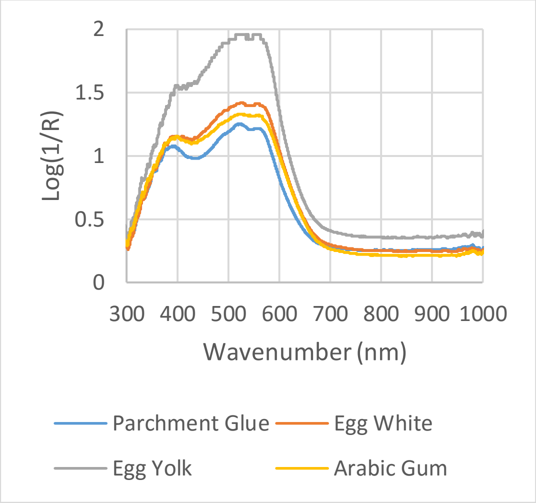

Figure AP I.14: FORS spectra of cochineal lake #3a

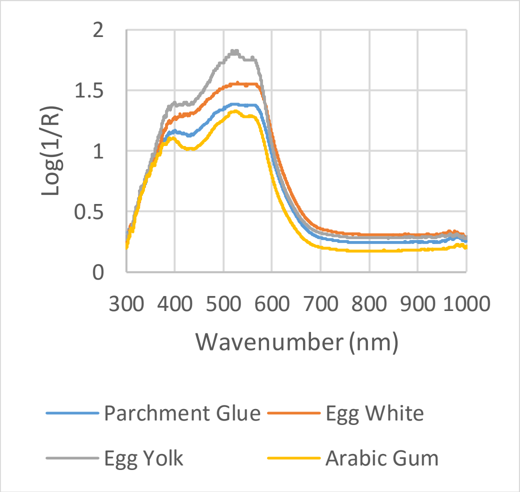

Figure AP I.15: FORS spectra of cochineal lake #3b

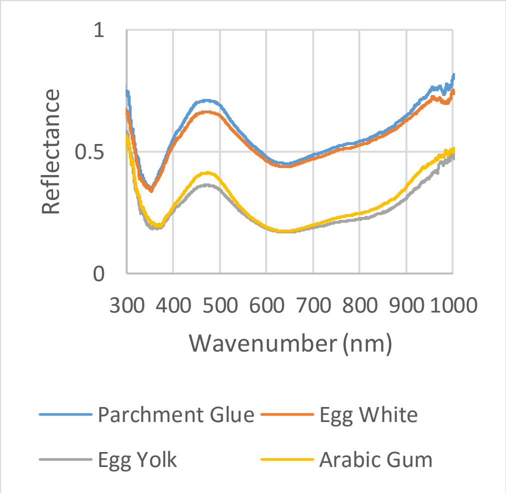

Figure AP I.16: FORS spectra of 90:10%wt, lead white : azurite.

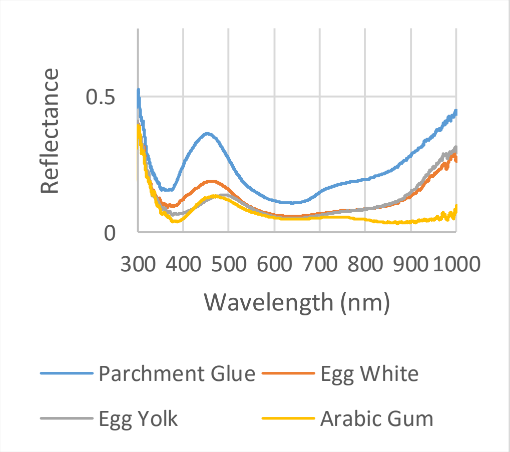

Figure AP I.17: FORS spectra of 90:10%wt, azurite : smalt.

APPENDIX II: MANIZOLA 116C ANALYSIS MAPS AND FORS SPECTRA

*f.*7r

Figure AP II.1: Left, analysis map of *f.*7r. Right, superimposed recto and verso.

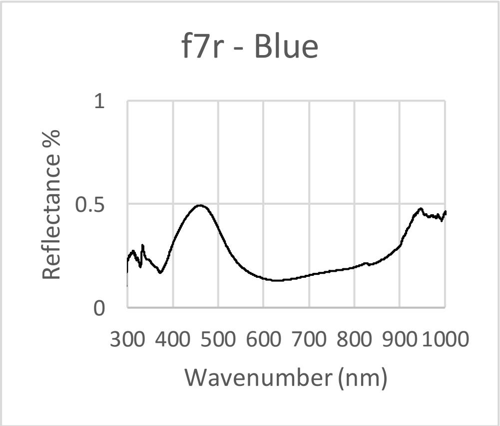

Figure AP II.2: FORS spectra of blue back ground of *f.7r*.

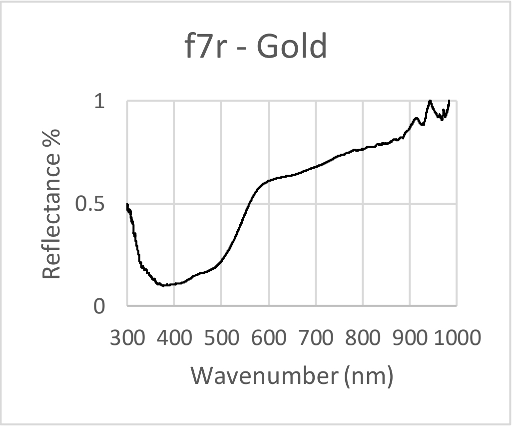

Figure AP II.3: FORS spectra of gold cheek of face on *f.7r*.

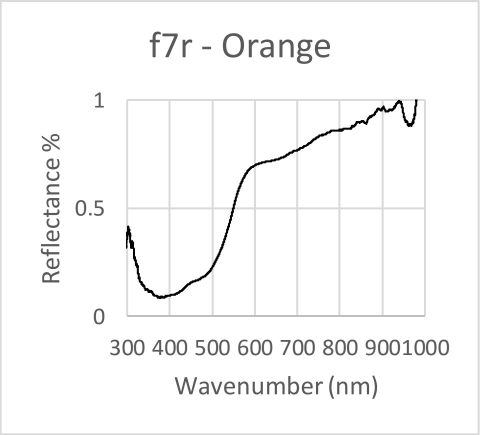

Figure AP II.4: FORS spectra of orange face on *f.7r*.

f.9v

Figure AP II.5: Left, analysis map of *f*.9v. Right, superimposed recto and verso.

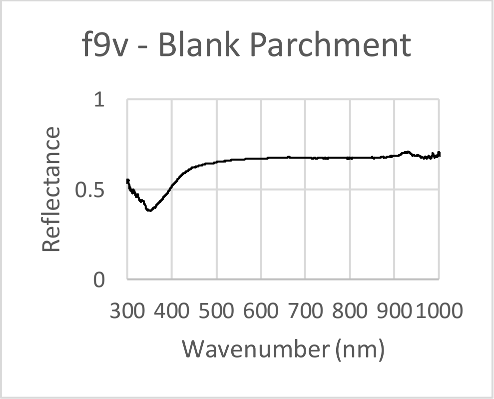

Figure AP II.6: FORS spectra of blank parchment of *f*.9v.

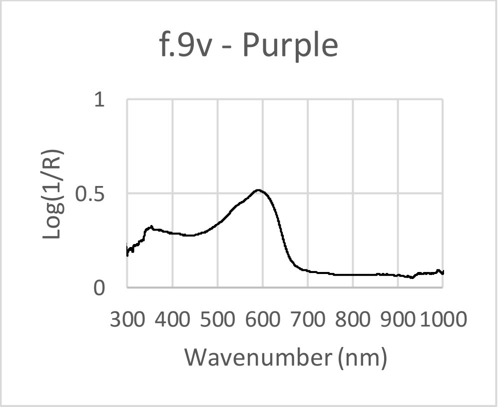

Figure AP II.7: FORS spectra of purple border of *f*.9v.

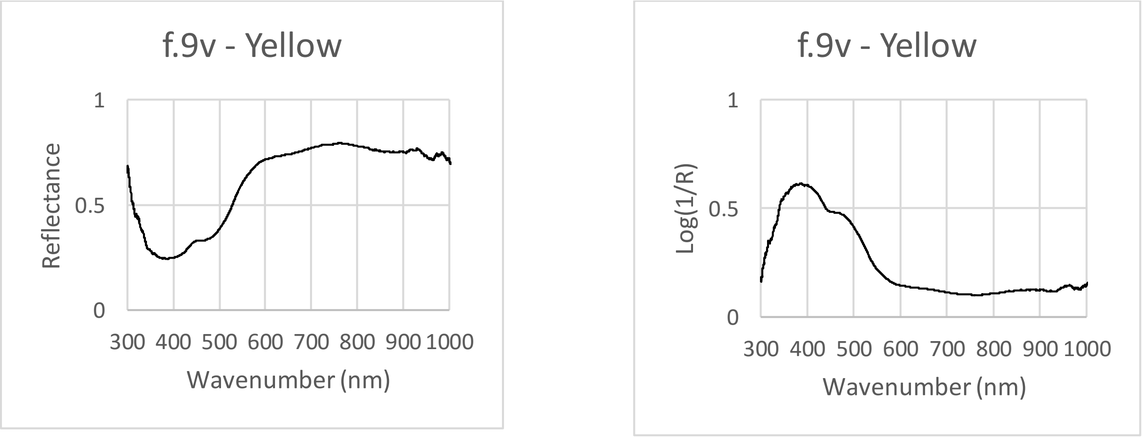

Figure AP II.8: FORS spectra of yellow background of *f*.9v
Left, reflectance. Right, apparent absorbance.

f.13r-a

Figure AP II.1: Left, analysis map of *f*.13r-a. Right, superimposed recto and verso.

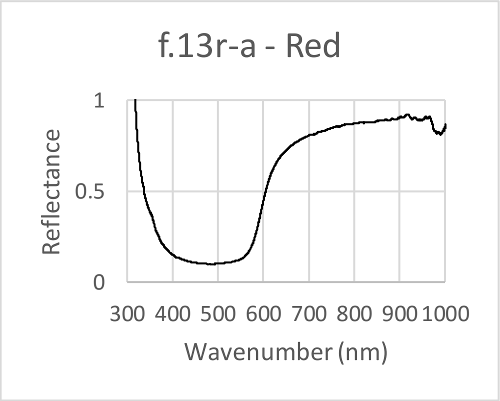

Figure AP II.9: FORS spectra of red background of *f*.13r-a.

Figure AP II.10:analysis maps of text on *f*.13r-a.

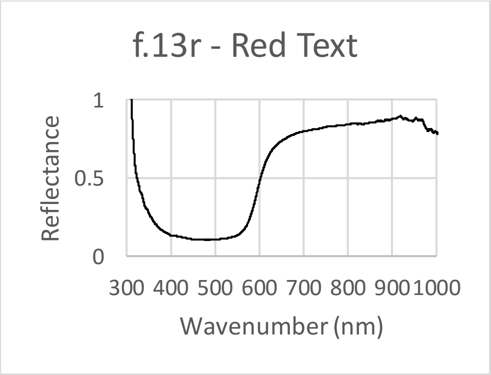

Figure AP II.11: FORS spectra of red text on *f*.13r.

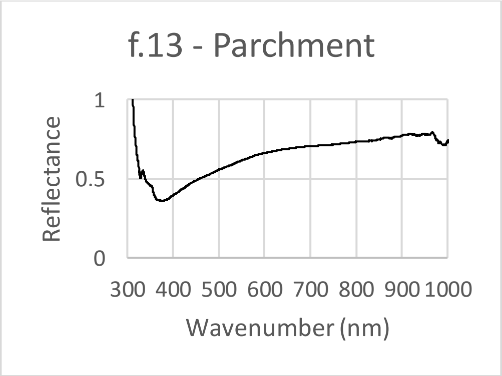

Figure AP II.12: FORS spectra of blank parchment on *f*.13r.

f.13r-b

Figure AP II.13: Left, analysis map of *f*.13r-b. Right, superimposed recto and verso.

f.13v-a

Figure AP II.14: Left, analysis map of *f*.13v-a. Right, superimposed recto and verso.

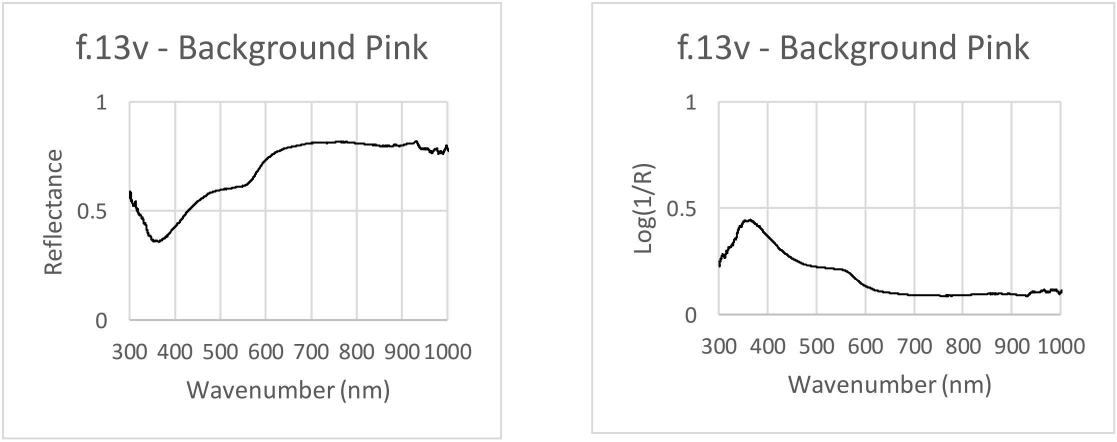

Figure AP II.15: FORS spectra of pink background of *f*.13v-a.
Left, reflectance. Right, apparent absorbance.

f.13v-b

Figure AP II.16: Left, analysis map of *f*.13v-b. Right, superimposed recto and verso.

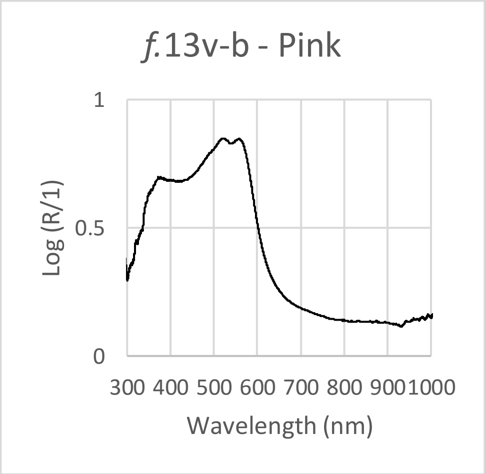

Figure AP II.17: FORS spectra of pink pigment on *f*.13v-b.

f.13v-c

Figure AP II.18: Left, analysis map of *f*.13v-c. Right, superimposed recto and verso.

f.14v

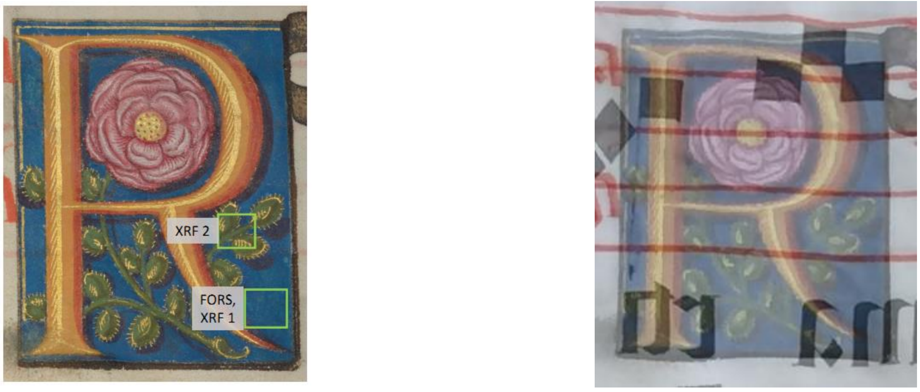

Figure AP II.19: Left, analysis map of *f*.14v. Right, superimposed recto and verso.

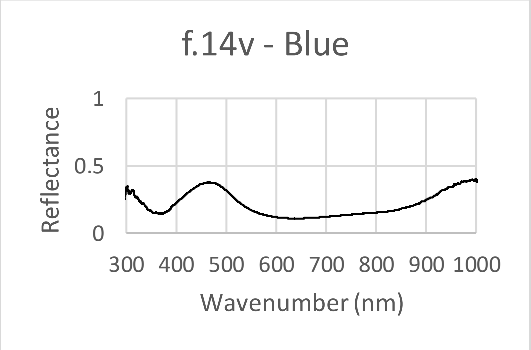

Figure AP II.20: FORS spectra of blue background on *f*.14v.

f.15v

Figure AP II.21: Left, analysis map of *f*.15v. Right, superimposed recto and verso.

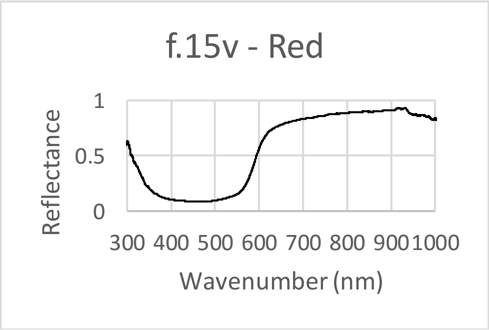

Figure AP II.22: FORS spectra of red background on *f*.15v-b.

f.31r

Figure AP II.23: Left, analysis map of *f*.31r. Right, superimposed recto and verso.

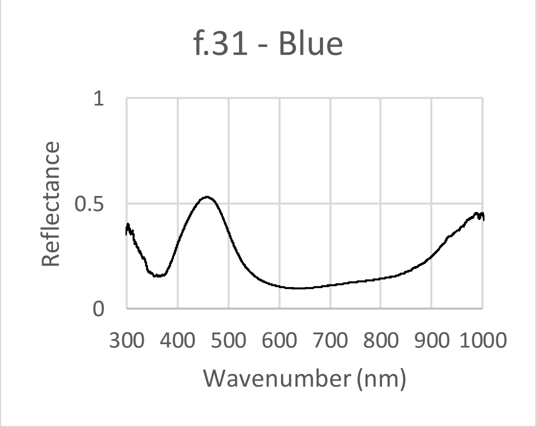

Figure AP II.24: FORS spectra of blue background on *f*.13v-b.

f.33r

Figure AP II.25: Left, analysis map of *f*.33r. Right, superimposed recto and verso.

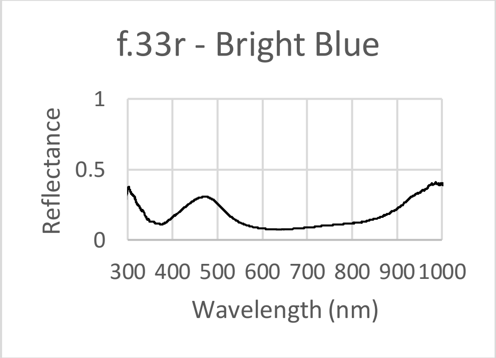

Figure AP II.26: FORS spectra of the blue background on *f*.33r.

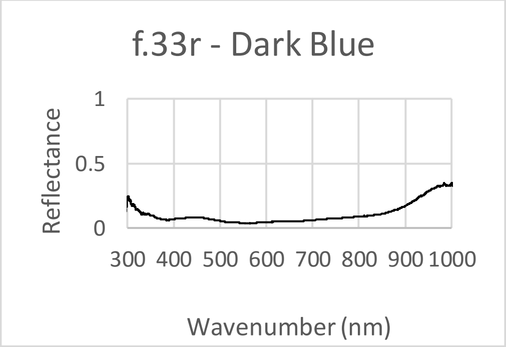

Figure AP II.27: FORS spectra of dark blue shadow on *f*.33r.

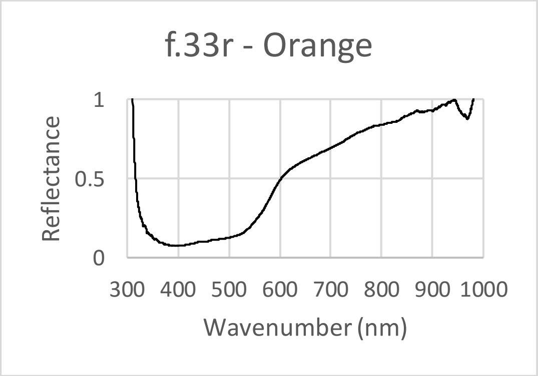

Figure AP II.28: FORS spectra of orange chest of figure on *f*.33r.

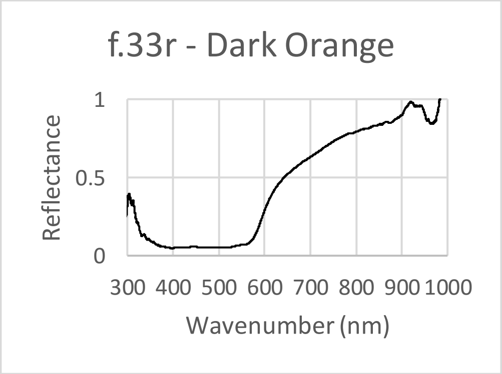

Figure AP II.29: FORS spectra of dark orange waist of figure on *f*.33r.

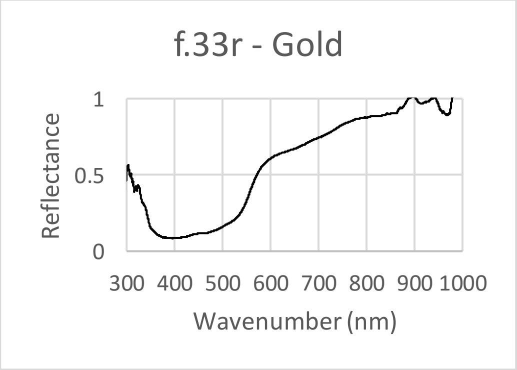

Figure AP II.30: FORS spectra of gold on figure on *f*.33r.

f.35r

Figure AP II.31: Left, analysis map of *f*.35r. Right, superimposed recto and verso.

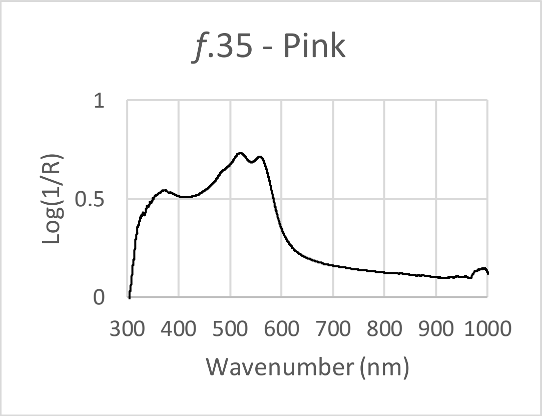

Figure AP II.32: FORS spectra of pink on *f*.35r.

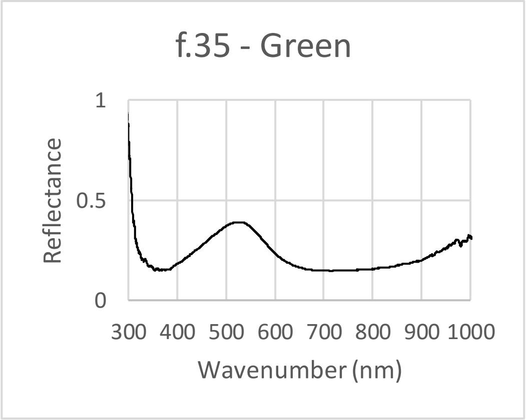

Figure AP II.33: FORS spectra of green background on *f*.35r.

f.37v

Figure AP II.34: Left, analysis map of *f*.37r. Right, superimposed recto and verso.

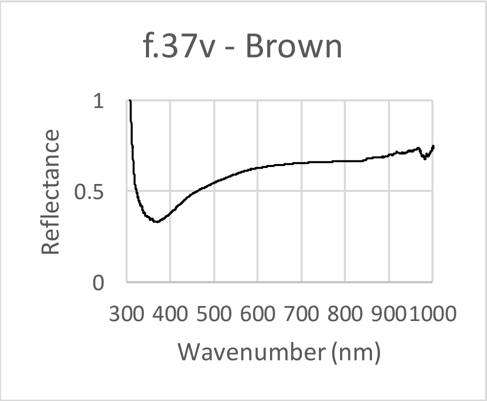

Figure AP II.35: FORS spectra of brown border of *f*.37v.

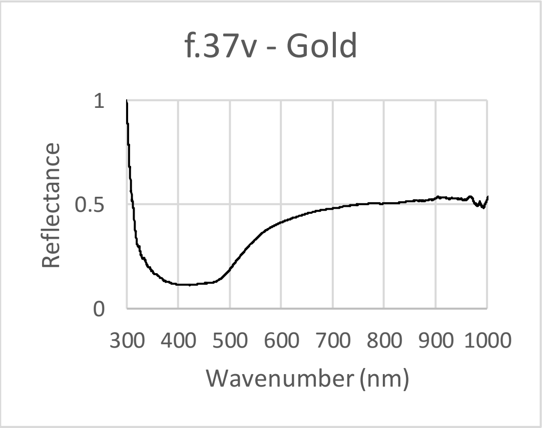

Figure AP II.36: FORS spectra of gold background on *f*.37v.

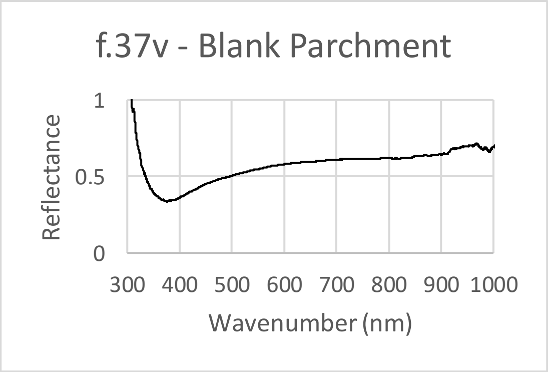

Figure AP II.37: FORS spectra blank parchment of *f*.37v.

f.39*r

Figure AP II.38: Left, analysis map of *f*.39*r. Right, superimposed recto and verso.

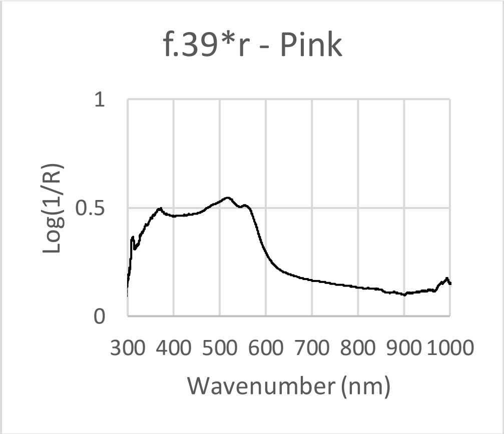

Figure AP II.39: FORS spectra of pink background of *f*.39*r.

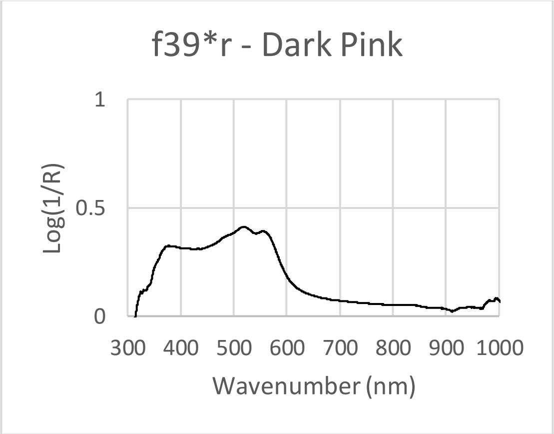

Figure AP II.40: FORS spectra of pink shadow of *f*.39*r.

f.41v

Figure AP II.41: Left, analysis map of *f*.41v. Right, superimposed recto and verso.

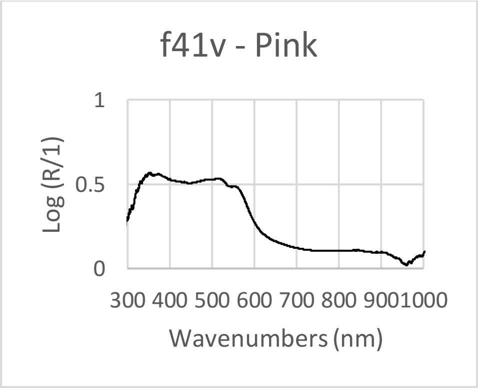

Figure AP II.42: FORS spectra of tail of figure on *f*.41v.

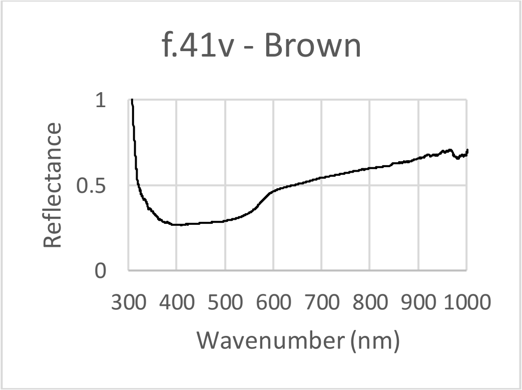

Figure AP II.43: FORS spectra of brown of the figure’s beard on *f*.41v.

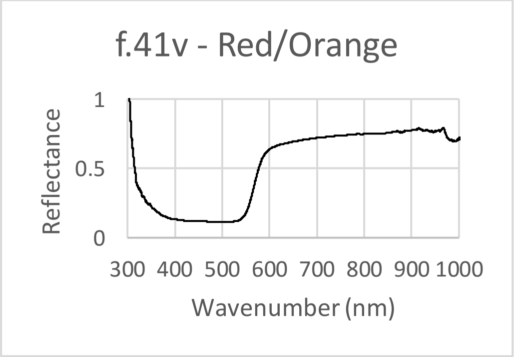

Figure AP II.44: FORS spectra of red/orange legs of figure on *f*.41v.

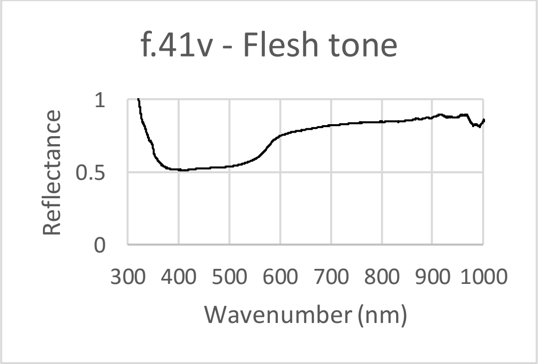

Figure AP II.42: FORS spectra of flesh tone of figure on *f*.41v

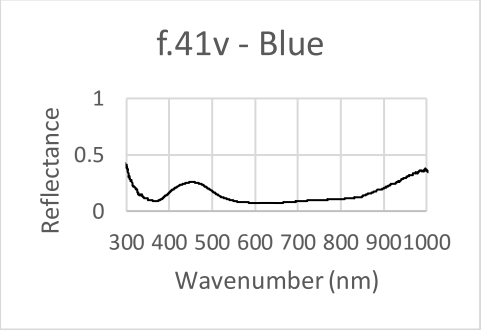

Figure AP II.43: FORS spectra of blue tail of figure on *f*.41v.

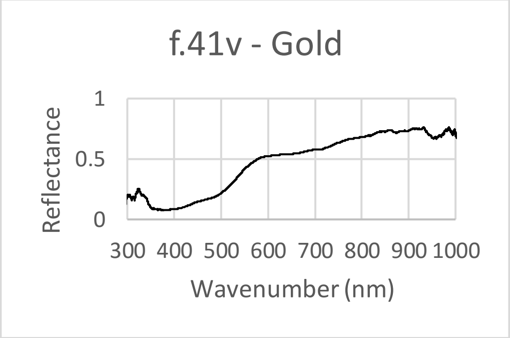

Figure AP II.44: FORS spectra of gold decorated background on *f*.41v.

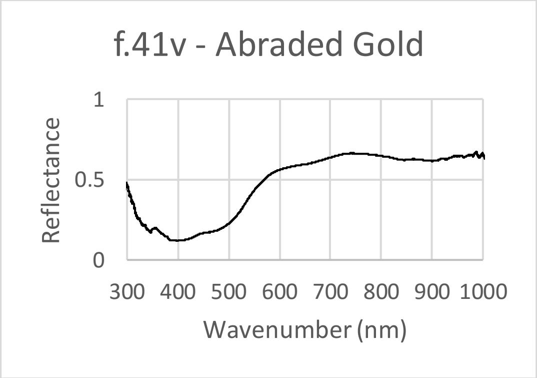

Figure AP II.45: FORS spectra of abraded gold background on *f*.41v.

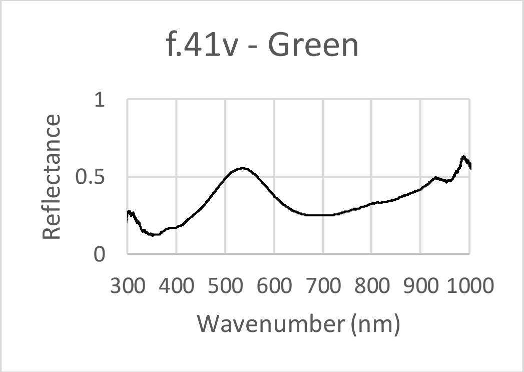

Figure AP II.46: FORS spectra of green tail of figure on *f*.41v.

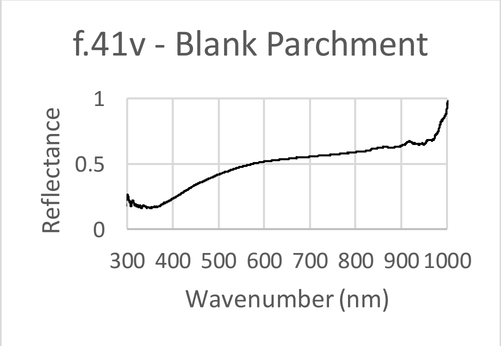

Figure AP II.47: FORS spectra of blank parchment of *f*.41v.

f.42v

Figure AP II.48: Left, analysis map of *f*.42v. Right, superimposed recto and verso.

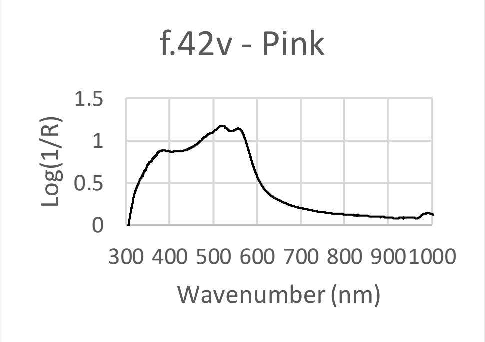

Figure AP II.49: FORS spectra of pink drapery on *f*.42v.

f.48v

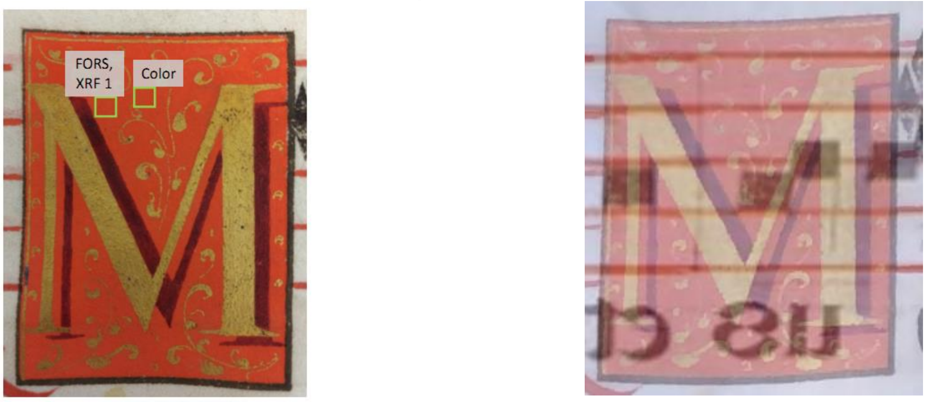

Figure AP II.50: Left, analysis map of *f*.48v. Right, superimposed recto and verso.

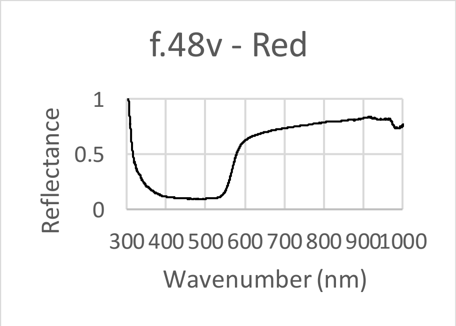

Figure AP II.51: FORS spectra red background on *f*.41v.

f.50r

Figure AP II.52: Left, analysis map of *f*.50r. Right, superimposed recto and verso.

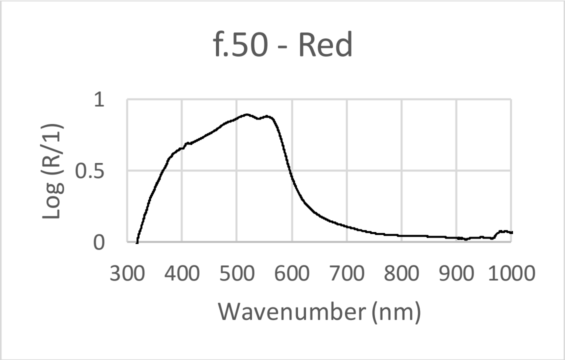

Figure AP II.51: FORS spectra of red background of *f*.41v.

f.53v

Figure AP II.52: Left, analysis map of *f*.53v. Right, superimposed recto and verso.

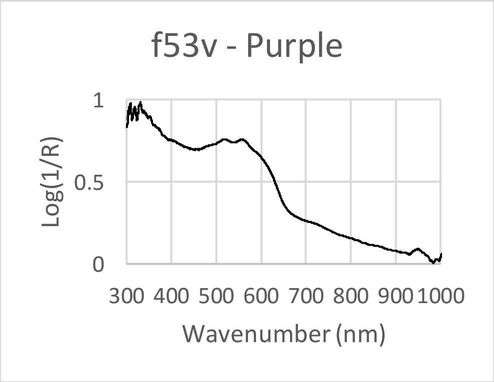

Figure AP II.53: FORS spectra of purple background of *f*.53v

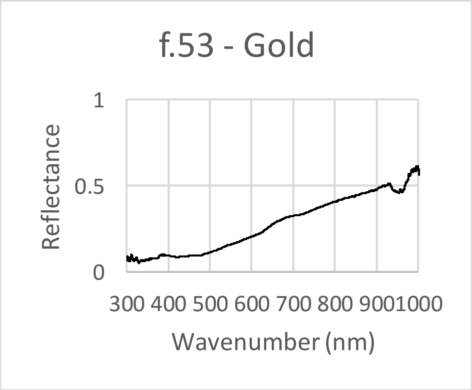

Figure AP II.54: FORS spectra of gilding on *f*.53v