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Treball Final de Grau

Study of the material and formal characterisctics of illuminated manuscripts from the XII-XVI centuries.

Estudi conjunt de les característiques materials i formals dels manuscrits il·luminats dels segles XII-XVI.

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Hi ha una força motriu més poderosa que el vapor, l'electricitat i l'energia atòmica: la voluntat.

Albert Einstein

Agraeixo al Dr. José Francisco García i al Dr. Xavier Saurina, pel seu suport constant al llarg del projecte, ja que m'han guiat i ensenyat en tot moment. De la mateixa manera, agrair als meus pares, al meu germà i als companys per fer més lleuger aquest temps.

I finalment al CRAI i a Neus Verger per les facilitats que ens han donat a l'hora de deixar-nos treballar amb el manuscrit.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

The sustainable development goals (SDGs), adopted by the United Nations (UN) in 2015, are 17 global interlinked goals with the objective of end poverty, protect the planet and improve the lives and prospects of all people by 2030. These goals are grouped into five axis known as the 5 Ps, being: people, planet, prosperity, peace and partnerships.

This paper focuses on the people axis in SDG 3, on people's health and well-being. Mental health is currently at the centre of an unprecedented global spotlight. Since the COVID-19 pandemic, it is undeniable that mental and emotional health issues are around us, and it is impossible not to see news about this issue each week. Linked to people's mental health and society, art is one of the best ways of expression that humanity has had since its beginnings. Nowadays, it seems that there is a tendency towards a simpler and more basic art, as a representation to the society in which we live, as we want everything less complex to understand and as quickly as possible.

Here, we want to understand the creation process of manuscripts from the 16th century, bringing us closer to the working life of the scribes and illuminators of the time and get an idea about how they behaved as a society. A society very different from today's one, either from the way they were organised, to the scarce communication they could have with people outside their environment. In that sense, if we are able understand how ancient societies functioned by the study of art, we may can guide our own towards a better world.

It is not too late to achieve the 2030 goals and art can have an important role, apart from helping with mental and emotional health, art can help people to become aware of the consequences of not meeting this agenda. With art we can make representations of the future that awaits us, and in this way, make people aware of the path that we all have to take as a society to guarantee the human rights of all.

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1. SUMMARY

Although manuscripts are one of the few sources of information we have about our ancestors, there is a great lack of information about them. Within manuscripts there is a category known as illuminated manuscripts in which the text is accompanied by decorations with metals, such as gold or silver.

Due to the lack of techniques and materials at the time, the artists responsible for these works were few and far between, and all of them had very well-defined rules for their work.

The main objective of this work is to carry out a study of the chemical composition of the inks of the decorations and the formal characteristics of the illuminated manuscript Liber Horarum, Ms.1859, from the CRAI of the University of Barcelona, dated between the end of the 15th and the beginning of the 16th century and written in the area of Flanders. The first part of the study will be carried out using the X-ray fluorescence technique (XRF) to determine the pigments used, while the second part of the study will consist of parameterizing the most relevant formal categories of the manuscript.

Once the manuscript has been studied, a chemometric study of the chemical compositions and a formal study will be carried out in order to determine the number of techniques used in the production of the manuscript.

Keywords: Manuscript, chemical composition, formal characteristics, chemometrics.

2. RESUM

Encara que els manuscrits són una de les escasses fonts d'informació que tenim sobre els nostres avantpassats, tenim una gran manca d'informació sobre ells. Dintre dels manuscrits existeix una categoria coneguda com a manuscrits il·luminats; són aquells on el text ve acompanyat per decoració amb metalls com l'or o la plata.

A causa de la manca de tècniques i materials de l'època, els artistes encarregats de fer aquestes feines eren escassos i tots ells tenien unes normes molt definides a l'hora de fer el seu treball.

L'objectiu principal d'aquest treball consisteix a fer un estudi de la composició química de les tintes de les decoracions i de les característiques formals del manuscrit il·luminat Liber Horarum, Ms.1859, del CRAI de la Universitat de Barcelona, datat entre finals del segle XV i començament del XVI i escrit a la zona de Flandes. La primera part de l'estudi es durà a terme fent servir la tècnica de fluorescència de raig X (XRF), per tal de poder determinar els pigments utilitzats, mentre que la segona part de l'estudi consistirà a parametritzar les categories formals més rellevants del manuscrit.

Una vegada estudiat el manuscrit, es farà un estudi quimiometric de les composicions químiques i de l'estudi formal, per determinar el nombre de tècniques emprades a la realització del manuscrit.

Paraules clau: Manuscrit, composició química, característiques formals, quimiometria.

3. INTRODUCTION

Since the beginning of humanity, one of the objectives has been to preserve knowledge for future generations. Initially, this was done with cave paintings, until the creation of writing, when knowledge began to be written down in order to pass on information to future generations. Writing has undergone many changes throughout history; in its beginnings (3000 B.C.) writing consisted of symbols representing ideas, using the support of clay tablets, which evolved to the paper, passing through parchment. Today the physical support for writing is being abandoned, but the need to preserve existing manuscripts and the information they contain remains.

Manuscripts are handwritten documents on a support such as parchment and paper, among others. As writing spread around the world, so did manuscripts, which were used to write philosophical, scientific, literary and religious texts. They were at their height in the Middle Ages when copyist monks were responsible for their creation. Due to the great illiteracy of the time, this work fell to a very small group of people, who were responsible for the manufacture of the manuscripts, the preparation of the supports and the preparation of the inks.

3.1. PARCHMENT

The skins of different animals were used for the preparation of the parchments, the most common being those of goats, sheep and cows. As the skins were not used directly, they needed to be preserved by treating them with chlorine or potassium salts. In the case of dry skins, a little of these salts was simply added, and in the case of wet skins, they were immersed in saturated solutions of these salts for 4 or 5 days for preservation [1]. Before being handled, they were washed with water to remove the salts.

After this treatment, all the skins were first immersed in lime baths (the length of time depended on the thickness of the skin) to weaken the epidermis, the outer layer of the skin, and with the help of blunt tools, the skin was scraped to remove hair and flesh. After a water bath to remove the excess lime, the skin was spread with even tension and left to dry. At this point, it was scraped again to remove the thickest and innermost layer of the skin, the hypodermis.

Once all possible layers had been removed, it was treated with pumice stone to burnish it, to give it a shine [2]. Once the whole process was finished, a layer of clay or chalk, mixed with gum Arabic, was applied to fix it, and then egg white or linseed oil was applied to protect the surface from humidity.

This technique is thought to have begun in the 2nd century BC until the end of the Middle Ages when it began to be replaced by paper.

3.2. COLOURS

In terms of pigments, red was the colour with the most variants. Its most common production was vermilion (HgS). The other inorganic options were roasting white lead pigment (Pb_3O_4) or red ochre (Fe_2O_3). On the organic side, there was also a wide variety of compositions, the most common being grana, Brazilwood, and the preparation made from ivy or dragon's blood.

For white pigmentation, the use of lead has been the most common, to be more precise, $(PbCO_3)_2$-$Pb(OH)_2$. Other options, also used were chalk ($CaSO_4$-H_2O) and ashes from the calcination of shells.

Both organic and inorganic options could also be applied to the green hue. On the one hand, organic pigments were available from various plants, such as leeks and cabbages. However, the most commonly used variant for manuscripts was based on copper pigments, such as verdigris ($Cu(OH)_2$-$(CH_3COO)_2$-$5H_2O$), made from copper foil and vinegar, which, because of its corrosive effects, was harmful to the parchment. As a result, malachite green ($Cu_2CO_3(OH)_2$) came into use at the beginning of the 15th century.

Concerning the bluish hue, the use of inorganic pigments was far superior to organic pigments, the latter being extracted from plants such as indigo and pastel. The two most commonly used inorganic pigments were ultramarine blue $Na_{8\text{-}10}Al_6Si_6O_{24}S_{2\text{-}4}$ and azurite $Cu_3(CO_3)_2(OH)_2$.

As regards yellows, the most widely used, at first, was orpiment (As_2S_3), but due to its toxicity, it was replaced by organic dyes of vegetable origin, such as saffron or celandine. Centuries later, variants of inorganic yellow emerged, such as lead and tin yellow or dark ochre $Fe(OH)_3$ [3].

3.3. ILLUMINATED MANUSCRIPTS

One particular group of manuscripts, the illuminated manuscripts, are so called because of their illustrative decorations, either in the form of miniatures, scenes or capital letters decorated with gold or silver.

3.3.1. History

The earliest illuminated manuscripts date from the 4th century, when the Catholic Church began to decorate its religious texts with ornate initials and simple, sparse decorations, mainly focused on highlighting sacred words. Throughout the 6th and 7th centuries these manuscripts moved out of this sphere and began to be made for classical literature and certain scientific texts.

The vast majority of these manuscripts were made throughout the Middle Ages; during the High Middle Ages (7th-11th centuries) most of these elaborations were produced by monks and scribes. It was not until the Late Middle Ages (11th-15th centuries) that they started to become a commercial activity and scribes' and artists' workshops were established for this purpose. These objects were of great value at the time, due to their great artistic complexity, and historical and literary value. The use of precious metals, such as gold and silver, added extra value [4].

It was during the 11th and 12th centuries, when in regions such as France, England and the Holy Roman Empire, more illuminated manuscripts were produced, manuscripts that were still largely biblical in scope, although in each region they began to be done in a particular style. It was with the introduction of new styles, when miniatures began to be added, illustrations of a quality and detail, unique for the time, and where the profession of "miniaturist" emerged, who was the person in charge of making this type of decoration.

In the middle of the 13th century, this art had its greatest diversification, when different regional styles emerged, where we can rule out the Gothic, which achieved its maximum popularity during the 14th century. A style characterised by "more perfect" lines and the use of a more varied chromatic range that gave the colours more weight and symbolism. This art took hold in other European countries, such as the Netherlands, Spain and Italy, each with a distinct style, derived from its closest influences.

With the invention of the printing press in the 15th century, the production of all types of manuscripts declined until they were practically extinct, although there is evidence that they

were still being created throughout the 16th century. The importance of these manuscripts has transcended the centuries and they are now considered one of the most studied and admired objects of the Middle Ages.

3.3.2. Types of manuscripts

Due to the great popularity of illuminated manuscripts, they were taken to other areas of life outside the church. Although the most common were bibles, with depictions of the most mythical scenes from the Bible, there was also an increase in the number of manuscripts of books of hours, which were intended for personal prayer. They were often accompanied by biblical representations, prayers, psalms and liturgical calendars. Their decoration, apart from religious miniatures, consisted of floral decorations and ornamentation of materials such as gold or silver. Apart from the religious sphere, historical manuscripts and bestiaries, manuscripts with depictions and descriptions of animals and fauna were also illuminated.

Of the illuminated manuscripts that have survived to the present day, there are some remarkable ones [5]. Morgan's Crusaders' Bible, written around 1250, is peculiar in that it was made in the reverse order to the usual order, initially consisting of a manuscript that was only illuminated, without any text, which is why it is believed to have been intended to be as accessible as possible. In a later century, text was added to it, which makes it unique because of the order in which it was made.

The Westminster Abbey Bestiary, created around 1280, a bestiary with over 160 illustrations of depictions of both real and imaginary animals from the Bible.

The Liber Feudorum Maior, created along the XII and XIII centuries and located at the Archive of Aragon Crown, is the first non-religious illuminated manuscript preserved in Spain [6].

Related to the books of hours, the book of hours of Jeanne d'Evreux was written in Paris in the 1320s for the wife of Charles IV. It consists of 25 full-page illustrations and a total of 700 illustrations. The basic purpose of this manuscript was to be used for Christian prayer throughout the day. Its small size, smaller than a modern pocket book, makes it one of the most relevant books of hours today [5].

Another one that stands out for its peculiar beauty is The Black Hours, created in Bruges between 1475 and 1480 (see Figure 1) [7]. The uniqueness of this manuscript lies in its black-tinted leaves, which have been written in silver and gold ink, with images in blue. The use of this parchment and this technique of decoration is thought to have been exclusive to Bruges, as only

seven are preserved today, all in the Morgan Library & Museum in New York, although due to the use of inks for the colouring, their current state is not ideal, and this one in particular is in the best condition.

For many, however, the best illustrated book of hours is The Very Rich Hours of the Duke of Berry, written in France in two parts (see Figure 1). The first part was written around 1410, until the death of both the Duke of Berry and the artists. It was not until 1485 that the manuscript was discovered and was most likely completed by Jean Colombe [8]. The unquestionable skill of the author of this manuscript has made it the most famous book of hours to this day.

a b

Figure 1. (a) The Black Hours. Image from Wikipedia [7]. (b) Page from the calender of the The Very Rich Hours of the Duke of Berry. Image from Wikipedia [8].

3.3.3. Manuscripts in Spain

With regard to the illuminated manuscripts preserved in Spain, the collection from Catalonia stands out due to its large number of copies. Of this large collection, spread throughout the most important libraries and universities in the area, two manuscripts located in the Library of the University of Barcelona stand out, the Horae Divinae Ms.1841 and the Liber Horarum Ms.1859, the former from the convent of Sant Josep in Barcelona and the latter belonging to Gaspar Fuster [9] [10]. Today, both manuscripts are kept by CRAI. [11]

3.3.3.1. MS.1859

The Ms.1859 has the peculiarity of being a prayer book dated between the end of the 15th and the beginning of the 16th century, when its popularity was declining. A manuscript with Gothic calligraphy, where in the first 12 pages, there is a calendar with inscriptions of Flemish celebrations, which makes it have a connection with the Southern Netherlands, thanks to the presence of this calendar, we can approximate its dating.

Its origin is linked to the Belgian area of Flanders, due to the order of the prayers and the iconography, such as the setting of the miniatures, as well as its undeniable resemblance to works written in the region, such as the Manuscript Vat. Lat. 3770 (now in the Biblioteca Apostolica Vaticana, Vatican City) or Ms. 35313 (now in the British Library, London).

A manuscript with a structure based on margins marked with a thin red line to delimit the perimeter. Within this, there are Capital Letters of two sizes, one smaller with a single line and the other with two lines, decorated with gold leaf on a red background, within the text, written in black ink. Around this text are ornate initial letters with a matt-coloured background or with biblical miniatures inside them. The sides of the text are also decorated either with scenes, with floral decorations accompanied by insects, or on certain pages (15r, 25r and 112r) a mixture of both [9].

A book of hours that follows the order established by the religion, with supposedly three different artists, one in charge of the settings, one in charge of the miniatures of the capital letters and one exclusively for page 199v, The Flagellation of Christ, the latter page was added later and is in the Renaissance style. [9]

3.4. ARTOMICS

Artomics is a new scientific concept aiming at carrying out the study of art by combining compositional and formal analysis for subsequent chemometric processing. Thus, the analytical data generated can be processed very efficiently using methods such as principal component analysis.

For the analysis of the chemical composition of the illuminations, non-invasive and non-destructive techniques are needed that allows its application in situ. Because as much information as possible has to be obtained in the shortest possible time, so as not to damage the manuscript, there are very few analytical techniques that meet these requirements. Among the most prominent are Remote reflectance spectroscopy, at the visible or infrared ranges, Raman Spectroscopy, Fibre Optic Reflectance Spectroscopy (FORS), X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) [12].

3.4.1. XRF

X-ray fluorescence (XRF) spectroscopy is an analytical technique that will be used in this project. XRF can determine the elemental composition of many kinds of materials. Because the technique itself is non-destructive, it lends itself ideally to the study of works of art and cultural heritage objects. The XRF technique consists of irradiating the sample with X-rays. When a high-energy X-ray photon collides with an inner-shell electron in an atom and has enough energy to overcome the binding energy of that electron, the electron can be expelled. This leaves the atom in an excited state. In an attempt to stabilize the atom, an electron from a higher shell will move into the vacancy created in the lower shell. Because it was an X-ray photon that was initially absorbed by the atom, this process is called X-ray fluorescence.[13]

Two letters are used to classify each fluorescence line, the first letter describes the orbital where the hole was produced (K, L, M) and the second letter describes where the electron that occupies this hole comes from (α, β, γ, δ) [13].

Although it is an ideal technique for the treatment of cultural heritage objects, it has some implicit disadvantages. Once the sample has been irradiated, there is an important matrix effect when X-rays emitted, can be absorbed by other elements in the sample, which means that not all the energy reaches the detector, resulting in a lower signal than the real one. The geometry of the detector is also important to optimize the relationship between the incidence and detection angle of radiation. Some XRF instruments (as the used in this study) is specific for cultural heritage studies, nonetheless the size of the instrument head and the extreme care with which the manuscripts have to be handled, make impossible to be able to measure all the desired areas, in illuminated books that areas close to central part.

Finally, because the instrument has a limited sensitivity for elements of low atomic number, organic pigments are not detected.

Once the measurements have been made, the position of the signals and the area of the same allows the qualitative and semi-quantitative elemental analysis. For semi-quantitative analysis (as a consequence of the difficulties of modeling the matrix effect) a calibration of the data obtained will be necessary. Pymca provides tools and analysis methods for the transformation of the peak data obtained, to areas of the pigment composition elements. This data processing and the obtaining of more accurate and, in our case, more manageable results will facilitate further processing and analysis.

3.4.2. PCA

For the analysis of the data obtained, it will be necessary to use chemometric methods such as PCA for exploratory studies.

Briefly, PCA is a mathematical statistical technique that consists of reducing the dimensionality of the data. The operation of PCA is based on the creation of new variables that explain the greatest possible variation in the data, these variables are known as principal components (PCs). These PCs are ordered from highest to lowest representation of the variables, with the first PC explaining the greatest variability in the data, followed by the second, which must be orthogonal to the first, in order to describe the greatest remaining variance.

Once the principal PCs have been determined, the samples are represented in this new coordinate system. The new sample values are known as scores, and each sample has a score for one PC. These scores are formed as a linear combination of the original variables and the weight attributed to each variable, known as ``loadings'' [14].

4. OBJECTIVES

The aim of this study is to establish the chemical and formal characteristics of the miniatures and the support where they were made, in the Ms.1859. In order to achieve these objectives, the following specific objectives have been stipulated:

- Establish the conditions of measurement. Due to the use of a radioactive analytical technique, the measurement conditions will have to be established.
- Composition of the support and its reproducibility. To determine the composition of the support used and its reproducibility, by means of XRF.
- Composition of the miniatures. Using XRF measurements, establish the pigments used in the decorations.
- Establishment of the formal variables. Establish the most relevant formal variables of the manuscript.
- Establishment of the relationship between the different miniatures.

Both chemical and formal data will be pre-processed and analysed using chemometric tools.

5. EXPERIMENTAL SECTION

This work has been carried out entirely on Ms.1859; it was decided to separate the manuscript into 6 different parts: the support (parchment), the miniatures, the capital letters, the environment, the decoration of nature and the background where this decoration is located. As for the colour measurements, the following have been chosen: blue, green, pink, red, and yellow, in addition to the gilding. Although the initial intention was to take measurements of each colour in each different area/part, the impossibility of carrying out this idea, due to the lack of analysable points, has led to the need to make decisions in situ.

Analysis design included to carry out a quintuplicate of each colour in each zone within the same page, in order to be able to determine the reproducibility of the pigments. In addition to the quintuplicates within the same page, a minimum of one measurement was performed in other 5 pages to assess the reproducibility throughout the manuscript. Finally, a measurement was performed from each parchment where any colour measurements were done.

The miniatures refer to those illustrations (see Figure 2), generally of a religious nature, which occupy a space located in the margins within the text. The capital letters are those golden letters on a red background located on certain pages within the text. The surroundings and decorations (and therefore the backgrounds) are those that are located outside the text box, the former being representations of scenes and the latter decorations.

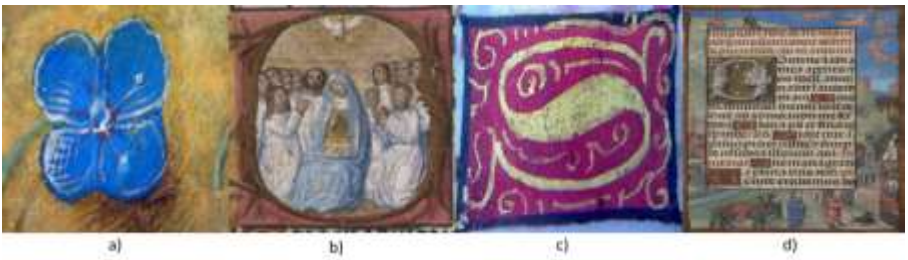


Figure 2. The different areas where the measurements have been made (a) Decoration, (b) Miniature, (c) Capital letter and (d) Environment.

5.1. XRF MEASUREMENTS

For the compositional analysis of Ms.1859, the ELIO spectrometer, a commercial portable instrument manufactured by XGLab, was used. The instrument uses a rhodium tube as X-ray source and the detector is derived from silicon, which allows a resolution up to 135 eV. This

equipment has an analysis range of 1 to 40 keV, making it possible to determine elements from Na to U. For the positioning of the X-rays, the equipment has a built-in camera and two light beams.

Some practical considerations concerning the XRF measurements are as follows: (i) The radiation penetrates the material and can reach the back and other sheets, so there may be interference; to avoid this problem, a layer of methacrylate of about 1.0 cm can be used between the page to be analysed and the rest of the manuscript. However, this does not prevent the radiation from detecting the verso at the measurement point, so it is necessary to look for areas where there is no decorative ink or lettering on the verso. (ii) The current state of Ms.1859 prevents a complete opening of the manuscript, which makes it impossible to take measurements on the internal parts of the leaves.

Since the X-ray source is rhodium and the instrument uses argon as an inert gas, these elements will always be detected with similar areas. This will allow them to be used as reference elements, in the event that, to some extent, the areas of these elements deviate from those of the other samples, they can be considered anomalous.

In order to determine on which page of the manuscript the measurement is made, all measurements will be numbered with the number of the page where it was made and an r or v if it refers to the recto or verso of this page (e.g. 25r refers to page 25 for the recto part and 25v for the verso part of this page).

Regarding the XRF working conditions, the following conditions were used a measuring time of 60 s, tube voltage of 50 kV and the tube current of 80 μA.

During the measurements, a portable microscope model QS.IR-940 with a magnification from 10-50x and 200x designed by Euromex, was used to take measurements of the details of the decorations. This microscope has an integrated IR camera, which allowed us to see the hidden details of the work.

To process the data, first of all, a graphic representation of the spectra will be made, as can be seen in the following figure 3:

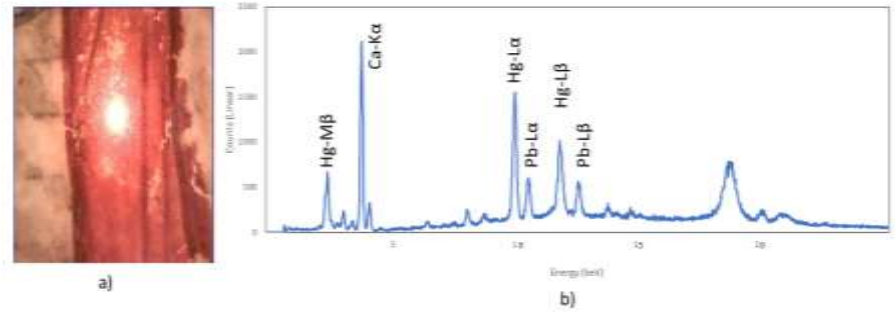


Figure 3. (a) Position where the average was taken and (b) Its spectrum.

With this information, we can extract the composition of the pigments and with the use of Pymca we can integrate the areas of the elements that can be associated to the quantitative information.

5.2. FORMAL DATA MEASUREMENTS

For the formal characteristics, it was decided to establish the following: text sides with decoration (3 or 4), peripheral natural, scene or mixed decoration, religious or domestic scene decoration, natural decoration with only flowers or flowers and insects, miniature of capital letter colour only, religious character, thumbnail in the space of the letter religious character, blue, pink, white or red flowers, green or white elements, green stems, gold/glossy or gold/toasted background, geometric perspective and golden lines on clothes.

5.3. DATA ANALYSIS

For the chemometric analysis, the chemometric software SOLO 8.6 from Eigenvector Research (Manson, WA, USA) was used. PCA was used as an exploratory method to evaluate the system behaviour and find out some sample and variable patterns.

In this study, the X-data matrix, will be composed by the different measurements made, where each row will be a different measurement and each column a different element, having a total of 26 elements.

For the formal categories, the decision was taken to apply binary values according to the presence or absence of the elements described by the categories on the different pages.

With these data, chemometric analysis was carried out using PCA, on the one hand, the formal characteristics and, on the other hand, the formal characteristics.

6. RESULTS AND DISCUSSION

This section will be divided into four sections: the composition of the different elements of the manuscript, the morphology of the decorations, the process of elaboration of the miniatures and the relations of the pages.

6.1. MEASUREMENT CONDITIONS

The thickness of the manuscript sheets is less than the penetration of X-rays under working conditions. This circumstance recommends, whenever possible, taking measurements in areas where the back of the sheet does not include other materials such as writing or other lighting. In addition, to avoid the integration in the spectrum of the information corresponding to different successive sheets, the analysis protocol includes the separation of the study sheet from the rest by means of a methacrylate plate 10 mm thick.

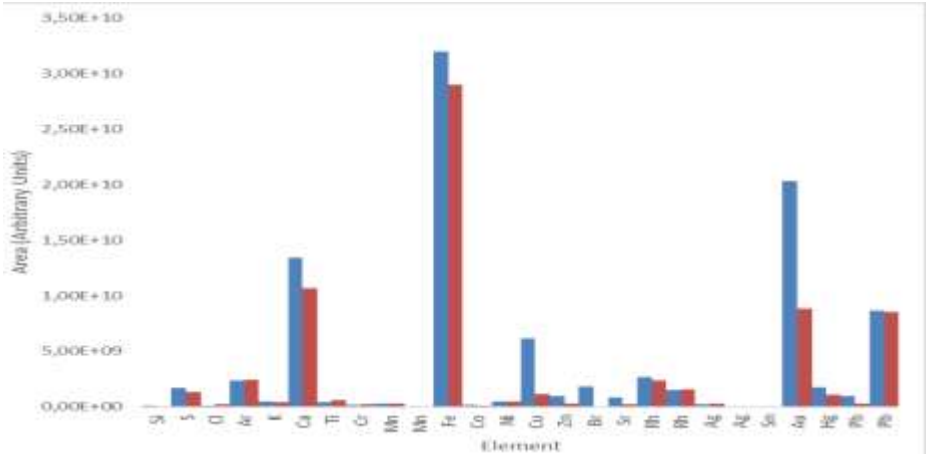


Figure 4: Comparison between measurements with (red) and without (blue) methacrylate.

In this Figure 4 it can be observed two measurements: the red including the methacrylate plate and the blue without it. It is clear the need to introduce the separation system in orther to get signals that only belong to the page under study. After highlighting the importance of correctly performing the measurements, the same protocol was always followed as detailed before.

6.2. COMPOSITION

The first part will consist of a compositional analysis of both the support, the parchment, and the materials used for the decoration of Ms.1859.

6.2.1. Parchment

The analysis of the parchment support can provide two pieces of information of interest: the first, if any of the sheets has been made with a different parchment and, the second, to know the composition of the support to improve the interpretation of the results of the analysis on the illustrations.

6.2.1.1 Composition

The spectra obtained from the measurements of the parchments showed that the composition of parchments include as main element is calcium (signals from radon and argon come from the XRF source). Iron, chlorine, potassium and lead also stand out in the composition of the scrolls.

Since the parchment are organic and XRF does not give signals for these elements, it is logical to find only elements from their treatment (see Figure 5). As explained in the section 3.1, the parchments were soaked in lime for several days to facilitate the subsequent removal of hairs, which is why calcium is detected. Another option is that they come from the use of chalk, which was used as a bleaching agent for parchment. Another method for removing other layers of hair was to use potassium or sodium chloride and then scrape the skin with an iron tool, this procedure would explain the presence of both chlorine and potassium, it should be remembered that sodium is not detected because it is an element with a very low atomic number, and iron would be explained by the use of the tools used. The presence of lead is also detected in the parchment, this element probably comes from involuntary spread along the centuries of some original materials as the lead white.

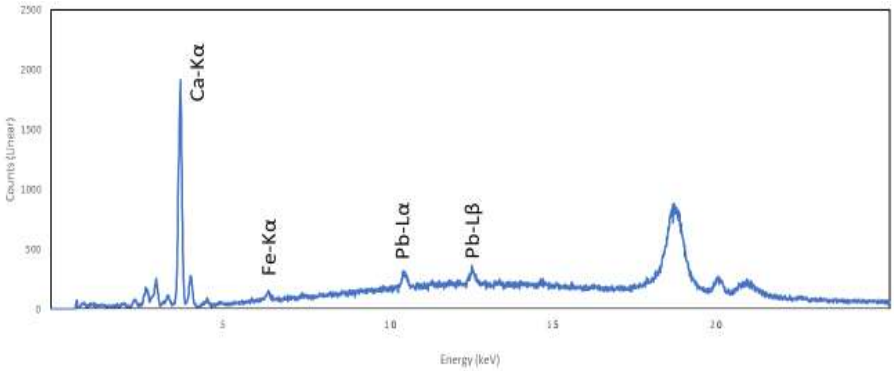


Figure 5. Measured spectral point on parchment.

6.2.1.2 Reproductibility

The natural origin of the parchment as well as the nature of its treatment suggests a heterogeneous distribution of the compounds. In the following Figure 6 it can be observed the area of potassium on the different pages. To quantify these dispersions, the percentage of RSD in potassium, throughout the entire parchment, is over 40% and the deviation within the same page varies from values above 30% on pages such as 15r, while on others, such as 69r, it is 12%.

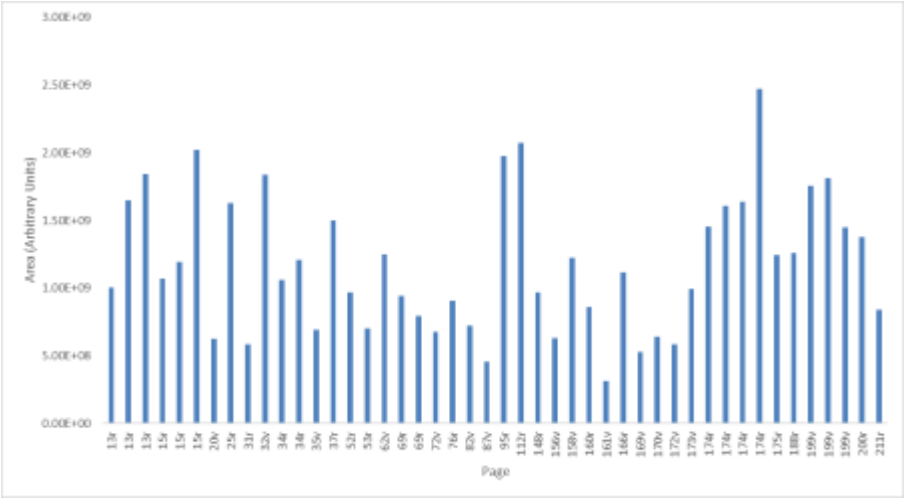


Figure 6. Representation of potassium in parchment.

It is interesting to observe that the RSD %, see Figure 7, of page 199v has a much lower than the others. This could be explained by the reduction of the particle size used for the treatment of the parchments and a better distribution. This fact points out that this page has followed a process different to the other included in the manuscripts. On the other hand the lack of reproducibility of Iron in page 174r is also higher than the rest, this could be related to the fact that on this page it was observed that ink had carried over from the next page.

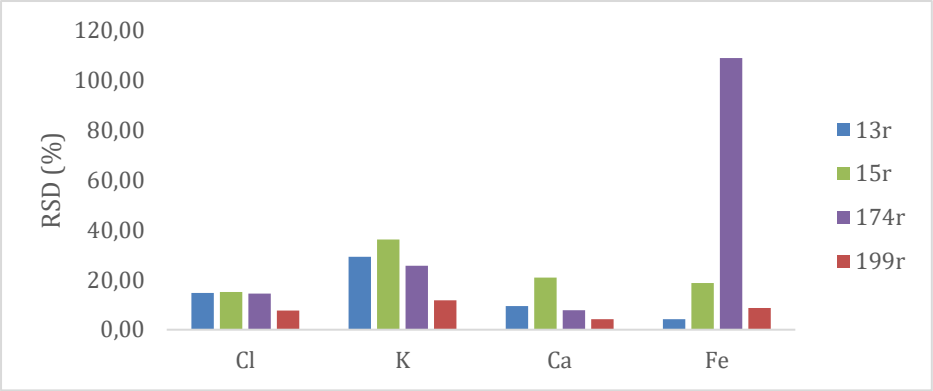


Figure 7. Representation of RSD at different locations in the manuscript.

6.2.2. Chromatic range

The analysis of the different points on the different decorated parts has allowed to identify the elemental composition of the coloured materials used in the manuscript. The following table 1 summarizes the information obtained.

Colour	Elements	Pigment	Area
Red	Hg	Vermilion	Surrounding, decoration
	Pb	Roasted lead white	Miniature
	Hg with Au	Vermilion	Capital Letters
	Organic	Organic	199v
Blue	Cu	Azurite	Surrounding, decoration, miniature
	Organic	Organic	199v
Light Yellow	Cu, Fe	Dark Ochre	Background
Matte Yellow	Cu, Fe, (equal parts), Pb	Dark Ochre	Background
Green	Cu	*	Surrounds, decoration, miniature
Rosa	Organic	Organic	All
Gold	Au	Lamina	CL, Miniature
		Dust	Background

* Without further analysis the pigment cannot be specified.

Table 1. Pigments used for the elaboration of the decoration in Ms.1859.

From the table above, it has been possible to establish the chemical composition of most of the pigments used in the decoration of the manuscript. In some cases, it has not been possible to establish exactly all the pigments, which would require the use of additional techniques, but a change of pigmentation towards organic compounds, can be seen on page 199v.

6.2.3. Gilding

Gilding, together with silver gilding, are the characteristic elements of illuminated manuscripts. They are the most elaborate decorations of the period, which was a technological advance at the time. Throughout Ms.1859, which only has gilding, three different gilding techniques can be found, one for the backgrounds, one for the capital letters and one for the miniatures, the latter two being very similar.

Although with the XRF measurements it is not possible to determine the gilding technique, it is possible to explain the order of painting of the layers, due to the fact that when analysing a higher layer of paint, the signals of the lower layers diminish by attenuation of the materials located in upper layers. This, together with the information that can be extracted from the images taken with the microscope, gives a more precise idea of the techniques applied.

6.2.3.1. Capital letters and miniatures

In capital letters and miniatures, very similar techniques were used. With the microscope image, it has been possible to represent the process of creating the capital letters and the gilding of the miniatures, two practically analogous processes.

As can be seen in Figure 8, first a red rectangle was painted on the parchment, which was delimited with a black line. Finally, the gilding was added. This process was the longest and most difficult. Although it is not possible to know which technique was used, it can be deduced that it was a technique known as leaf gilding.

Figure 8. Representation of the creation of a capital letter.

This technique consisted, in the case of the upper CL, of applying a binder, such as fish glue, egg white or arabic gum, to the red background, which was used to make the figure. A thin layer of gold was then applied and pressed to stick to the binder.

Furthermore, if a graphical representation, see Figure 9, of the calcium detected in the measurements is made, it can be seen that in the measurements made in the gold areas, the area of calcium is smaller than the area when it is made in the red areas. This is due to the fact that the X-rays of the measurement do not penetrate as much into the parchment because there are more layers of paint, so it can be confirmed that the gold is on top of the red.

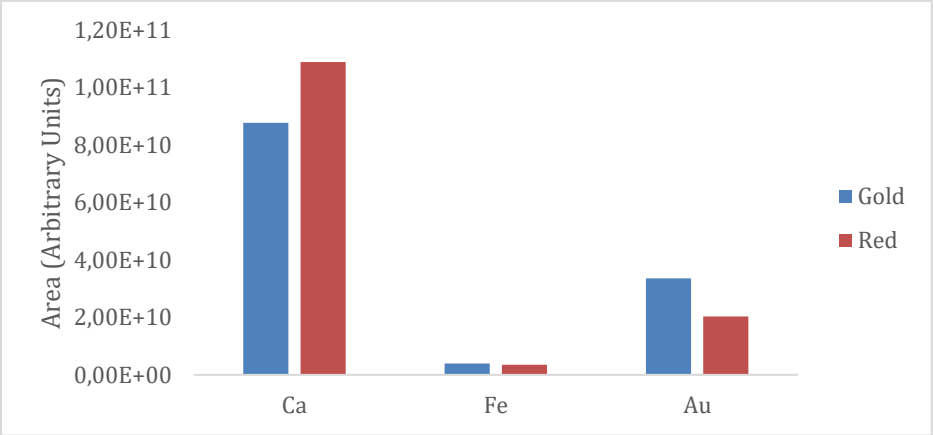


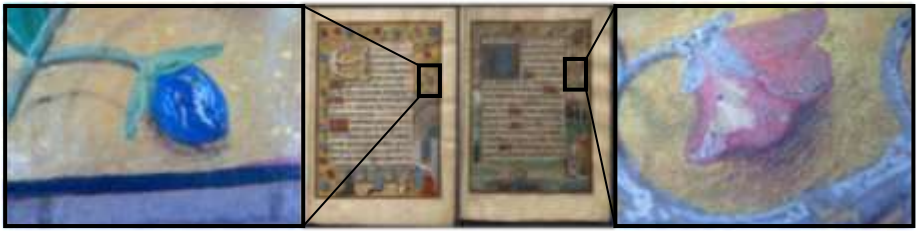
Figure 9. Representation of elements at two points of a capital letter.

The difference with miniatures, whose gilding technique is known as brush-point gilding, lies in the fact that in the latter, when the gilding is applied, it is done with gold ink. This ink was obtained by mixing gold powder with a binder, after which the figures were painted with a brush.

6.2.3.2. Backgrounds

The last gilding technique that can be seen is the bright yellow backgrounds. Two shades of yellow can be seen with the naked eye, see Figure 10, although with XRF measurements and images extracted with the microscope, gold particles can be detected.

This technique, known as gold ink, consisted of mixing gold dust with the paint. This meant that when the layer of paint was applied to the parchment, it already had the shine due to the gold.



a) b)

Figure 10: Microscope image of (a) golden yellow background and (b) tan yellow background.

6.3. MORPHOLOGY

One of the aims of this study is to categorise pages according to their formal characteristics. This is done in order to be able to group sets of pages with primary and secondary formal categories.

Formal variables are divided in two groups: the variables that refer to the overall decoration (such as the type of decoration found) and detail variables that focus on specific elements, such as the colour of the flowers or the insects represented. The following Figure 10, show the variables considered and the tables show examples of the variables, and table 2 and 3, show different examples of the variables.

Among the variables related to the overall decoration would be the number of decorated faces, the type of decoration represented or the typology of the miniatures, among other categories. Among the detail variables we include the colour of the decoration, the presence of insects or whether there is geometric representation.

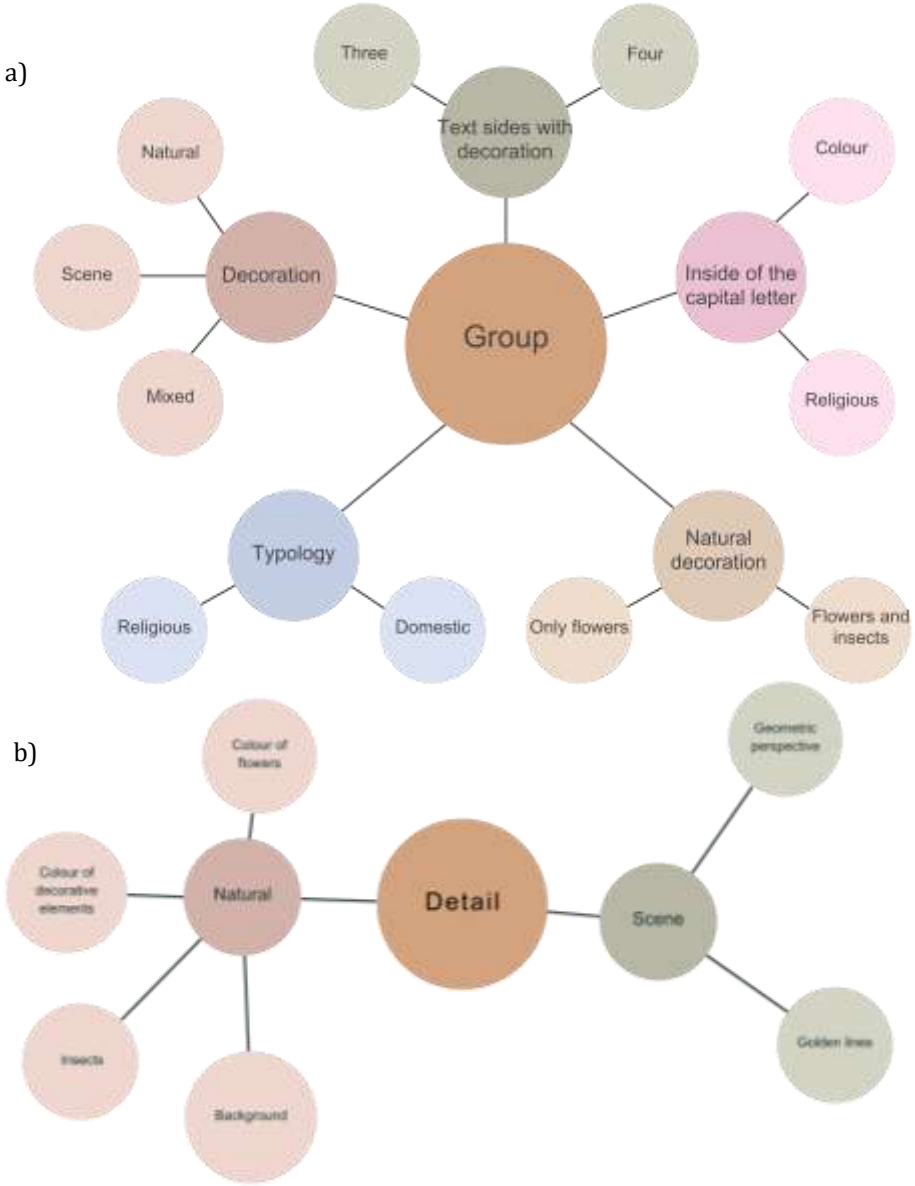


Figure 11. (a) Set variables determined (b) Detail variables.

Natural decoration	Scene decoration	Mixed decoration
		

Table 2. Types of decorations.

Red decoration	Red flower
	

Table 3. Difference between flower and red decoration.

6.4. CREATION PROCESS

The creation of the thumbnails should follow an established procedure. From the enlarged images obtained and the sequence of overlapping and superimposition of the materials, it is possible to make an approximation to the composition process of a miniature from the Ms.1859 book (see Figure 12). In this case, the miniature on page 172v.

Figure 12. Initial sequence of miniature creation

It should be noted that the gilding of the figure was added at this time, in the order in which it can be seen in the following sequence of images (see Figure 13).

Figure 13. Gilding process of clothes.

Finally it can be seen how it was decorated and the gilding process (See Figure 14).

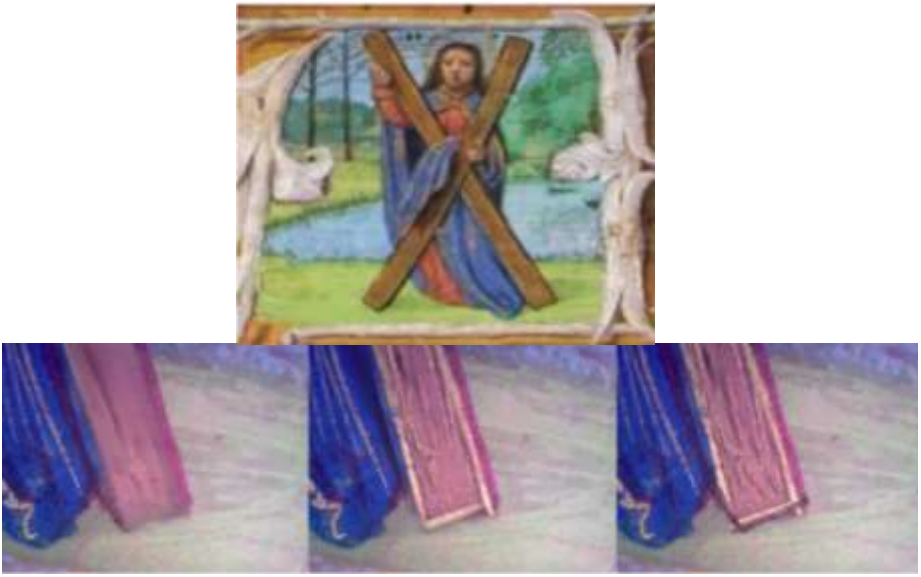


Figure 14. Final process of creation and gilding of a miniature.

6.5. EXPLORATORY STUDIES OF THE PAGES RELATIONSHIP BY PRINCIPAL COMPONENT ANALYSIS

This part of the report will focus on the study of the potential relationship of the different pages by using the chemometric results obtained from the compositional and formal analysis of Ms.1859.

6.5.1. Parchment

First, the parchments will be analyzed. Here, at least one measurement was obtained on each page, and on several of them, several measurements were made. The matrix to which the chemometric analysis will be applied consists of 76 measurements, spread over 35 pages, with 26 elements analyzed per measurement, in this case, PC1 represents 20.63% of the variance and PC2 10.90%. The scores graph (see Figure 15) represents a map of the pages while the loadings graph (see Figure 15) represents the variables, these being the elements analyzed

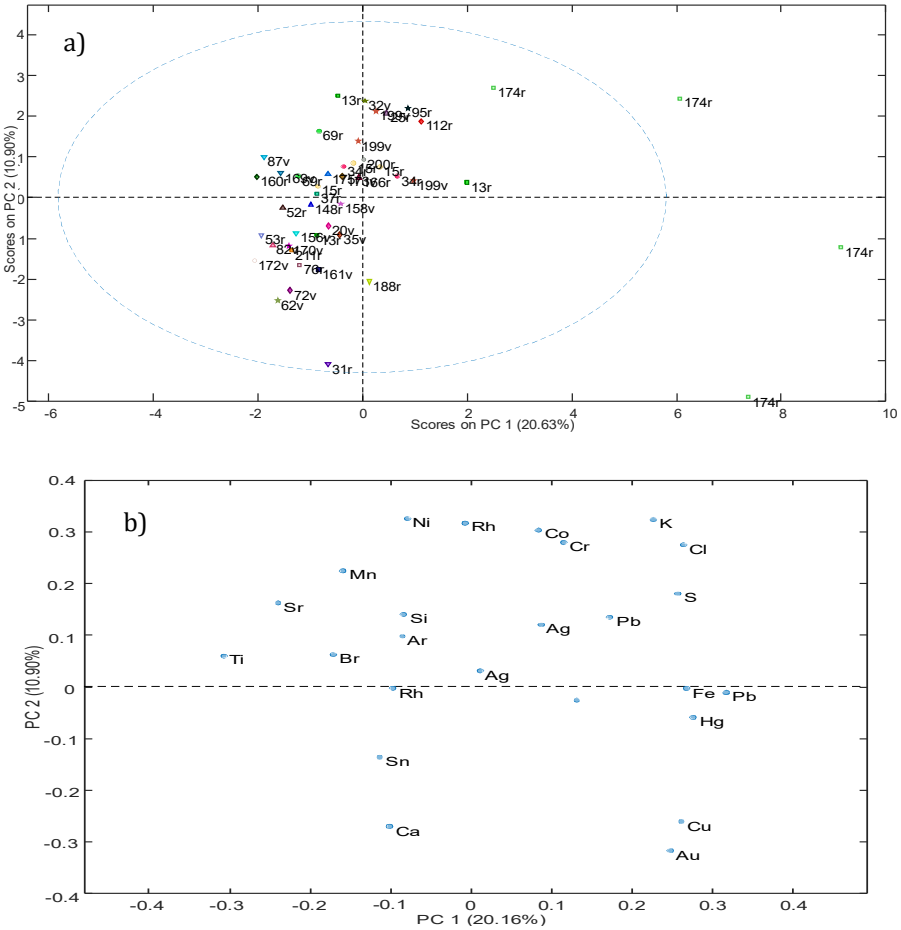


Figure 15. (a) Map of scores and (b) Map of loadings of the scrolls

Several conclusions can be drawn from the PCA on the parchments. The vast majority of the pages are indeed grouped, except for pages 31r, 188r and all measures of 174r. Observing the loadings, it can be seen that page 174r is directly influenced by Fe, Pb, Hg, Au and Cu, whereas the other two different measurements could be related to calcium. If a graphical representation (see Figure 16) of the elements of these different pages is made with respect to the average of the measurements (an average in which the different pages are excluded), the following graph is obtained.

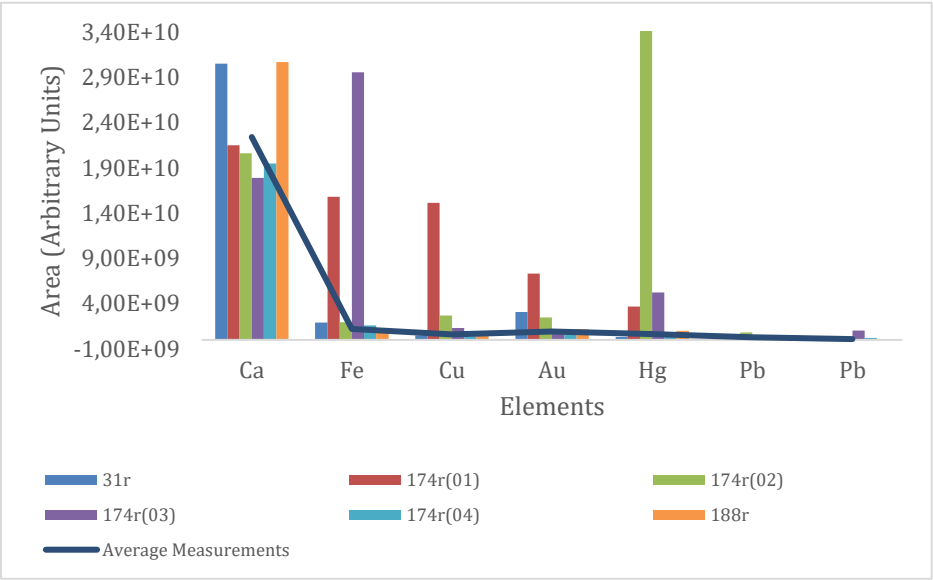


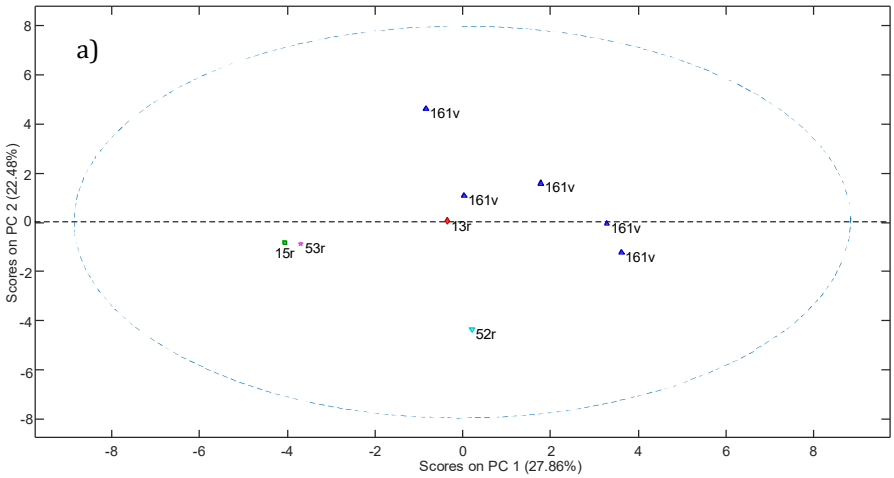
Figure 16: Representation of anomalous pages with respect to the average.

It can be seen that pages 31r and 188r contain a higher amount of Ca than the others. This can be explained by a different treatment received by these parchments or by some specific heterogeneity in this point, because just we have a single measurement of these pages. Concerning page 174r, it can be observed that several elements that differ, such as iron, copper, gold and mercury. To understand this, it is necessary to go to the manuscript and note that on this page, the verso (174r) is painted in brown and red on the back of the points where measurements 1, 2 and 3 were made. For this reason, point number 4 appears grouped with the rest of the points (see Figure 17). This result shows the ability to recognize points of different composition.

Figure 17: Page 174r and where the scroll was measured.

6.5.2. Gilding of capital letters

The gilding process of the CL's followed in this manuscript has already been explained above. The purpose now is to check if with the PCA of the gilded areas, it is possible to find noticeable differences to differentiate them. In this case, the matrix to be analyzed will consist of 9 measures, spread over 5 pages, with 26 elements per sample. In this case, PC1 contributes 27.86% of information to the system, while PC2 contributes 22.48% (see Figure 18).



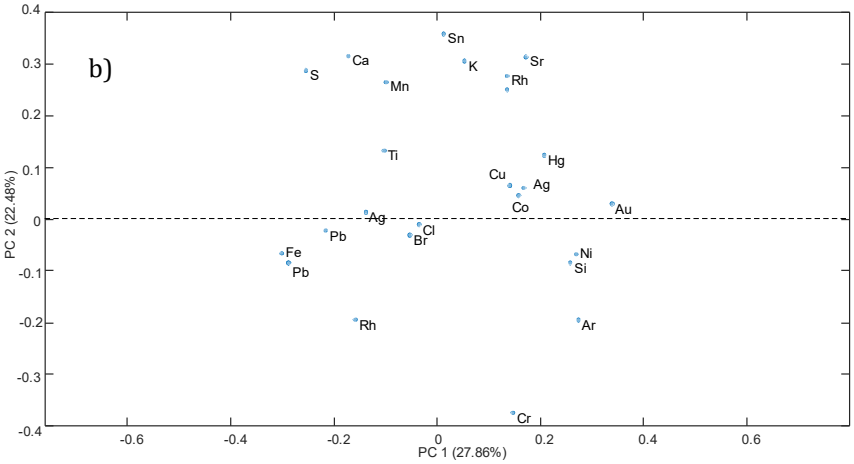


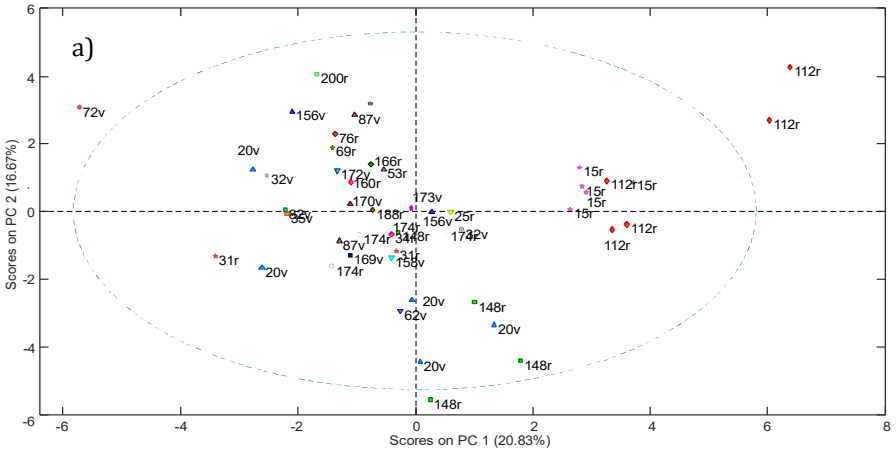
Figure 18. (a) Map of scores and (b) Map of loadings of gilding of CL

Thus, it can be seen how the measures 15r and 53r are different from the others, due to the gold absences.

6.5.3. Gilding of backgrounds

On analysing the backgrounds during production, the different tonality between them was observed. To be more precise, pages 15r and 112r have a mate yellow background tone, compared to the others, whose colour is bright yellow.

In this case, the matrix has a size of 52 measures by 26 elements, where the 3 main PCs represent 20.17%, 16.67% and 9.21% of the system respectively (see Figure 19).



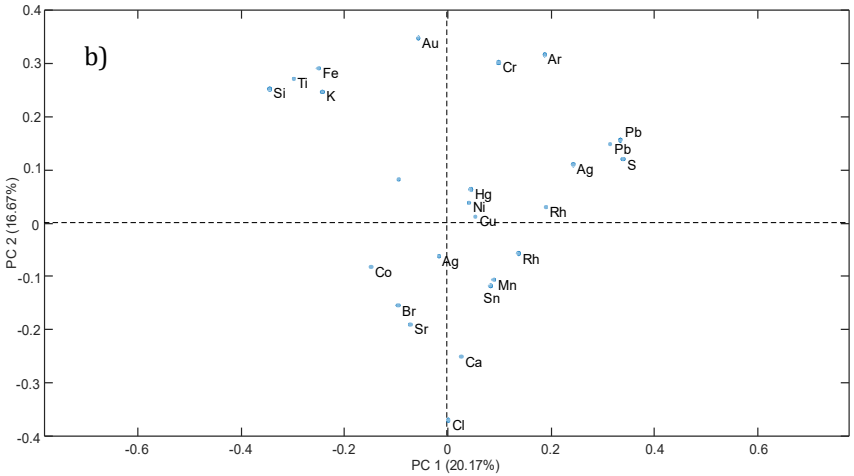


Figure 19. (a) Map of scores and (b) Map of loadings of gilding of backgrounds.

As can be seen in Figure 19(b) , in PC1 the weight of lead is important, where if we observe the distribution of the pages, page 112r and 15v are separated from the rest. On the other hand, page 72v is separated from the rest by the absence of lead and a high presence of iron. As far as PC2 is concerned, its importance is given by the gold, a gold applied with the technique described in section 6.2.3.2., present on all the pages. On the opposite side of PC2, we find page 62v and three replicas of 148r and 20v.

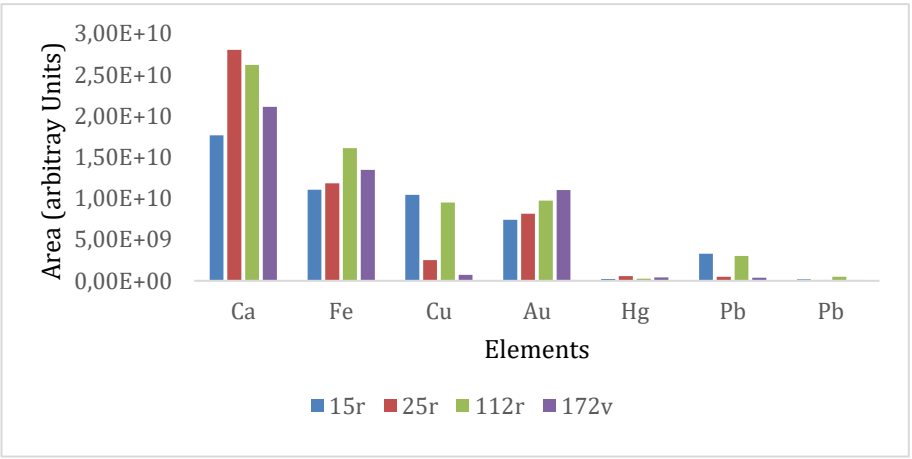


Figure 20. Area of elements on gold backgrounds

A graphical representation (see Figure 20) of the area of the elements on certain pages confirms that pages 15r and 112r have a high presence of lead and copper, even though they also contain gold. This may mean that to this mixture of yellow with gold. The darkening of the lead white or the copper compounds could be related with the darkening of the yellow in these pages.

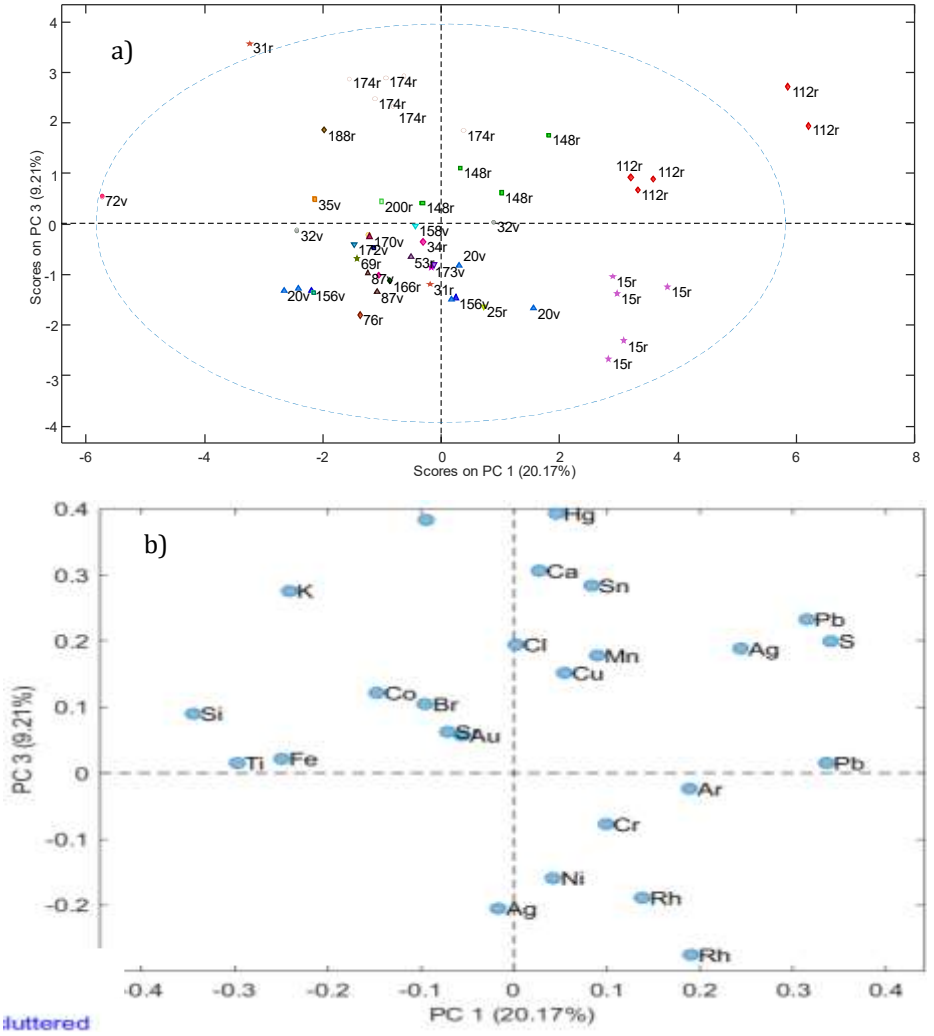


Figure 21. (a) map of scores and (b) map of loadings of gilding of backgrounds

If we finally add the information of PC3 with respect to PC1, see figure 21, we can see how PC3 separates the measurements by calcium concentration, which allows us to separate pages 112r and 15v between them. As for the measurements that used to be slightly separated, now it can only see how the measurements of page 148 are grouped together, unlike before. It is known that the 174r measurement is separated due to the presence of copper that has crossed the parchment and the 31r is a possible anomalous value due to the lower values of Rh and Ar.

6.5.4. Colours

6.5.4.1. Blue

For the blue zones analyzed, a matrix of 42 measurements was processed, on 16 pages, with 26 elements per measurement. In this case, PC1 represents 29.35% and PC2 17.43%.

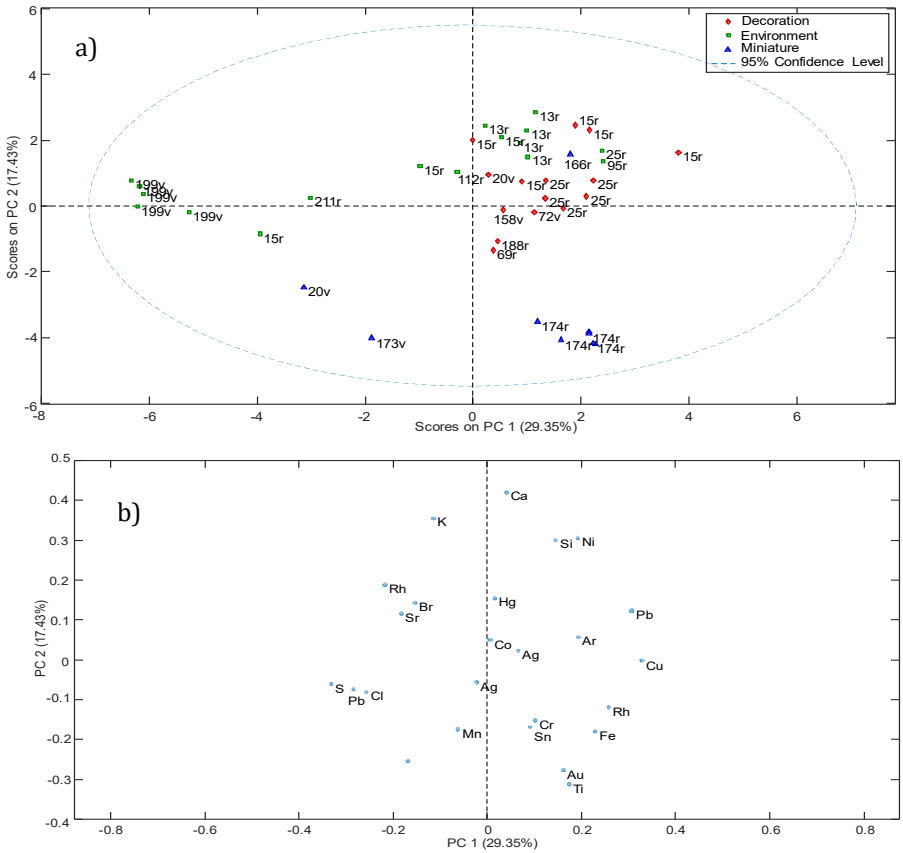
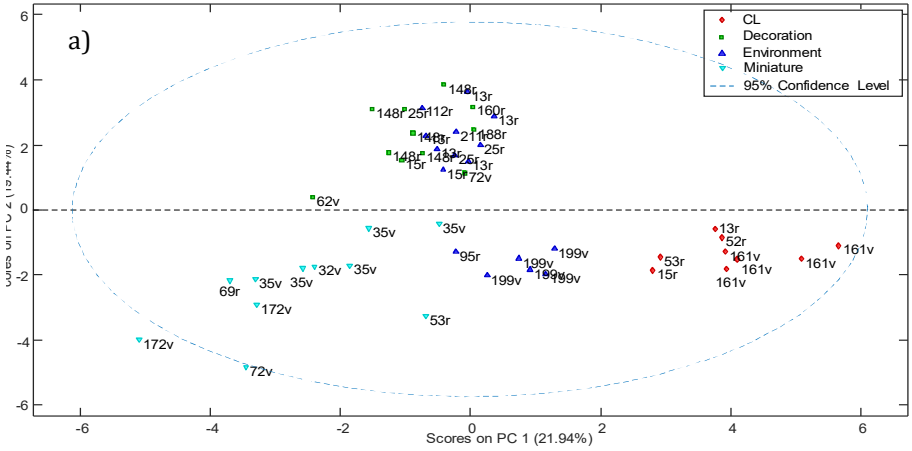


Figure 22. (a) Map of scores and (b) Map of loadings of blue.

On these results, (see Figure 22) it can be commented that PC1 is given by the concentration of Cu, page 199v being the one with the lowest concentration. PC2 is differentiated by two elements, Ca on the one hand and Au on the other. These elements help to differentiate the miniatures (page 20v, 173v and 174r) from the other measurements, because when the measurements were made on the miniatures, it was impossible to be near gold zones, except for the measurement on page 166r where it was not made in the outer zone and there was no presence of gold. It is worth mentioning that the measurement on page 15r and 211r, even though it is an analysis of the environments, has a close resemblance to the pigmentation on page 199v.

6.4.4.2. Red

In this case, the matrix used will have dimensions of 47x26, where the two main PCs will account for 21.94% and 19.44%.



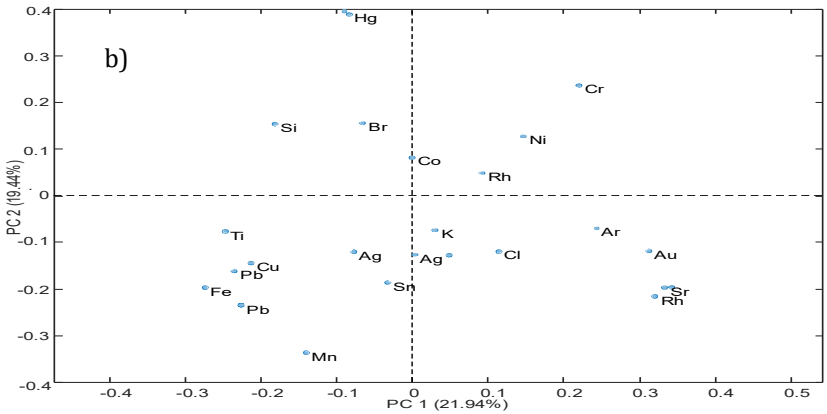


Figure 23. (a) Map of scores and (b) Map of loadings of red.

As can be seen in Figure 23, in PC1 the majority weight comes from the gold, which was only found in the capital letters. This red does not belong to the red ink, but it is due to the fact that the XRF spot has a dimension of 1 mm2 and there is no area of this size without the presence of gold. At the other end of PC1, there is lead, just in the area where the measurements of the miniatures are located, suggesting that minium was used for the miniatures. On the PC2, it is observed that the mercury has a greater weight, making that the measures of the decorations and of the environment are separated, with which it can be understood that in these decorations vermilion was used. Finally, it can be observed that page 199v is not grouped with anything and seeing its composition, it would suggest that an organic pigmentation was used. In addition, page 95r is close to a pigmentation similar to that of page 199v and page 62v, which was considered decoration, seems to have a pigmentation more similar to those of the miniatures.

6.5.4.3. Green

Here the matrix has dimensions of 26x26, where PC1 represents 35.85% and PC2 15.71% (see Figure 24)

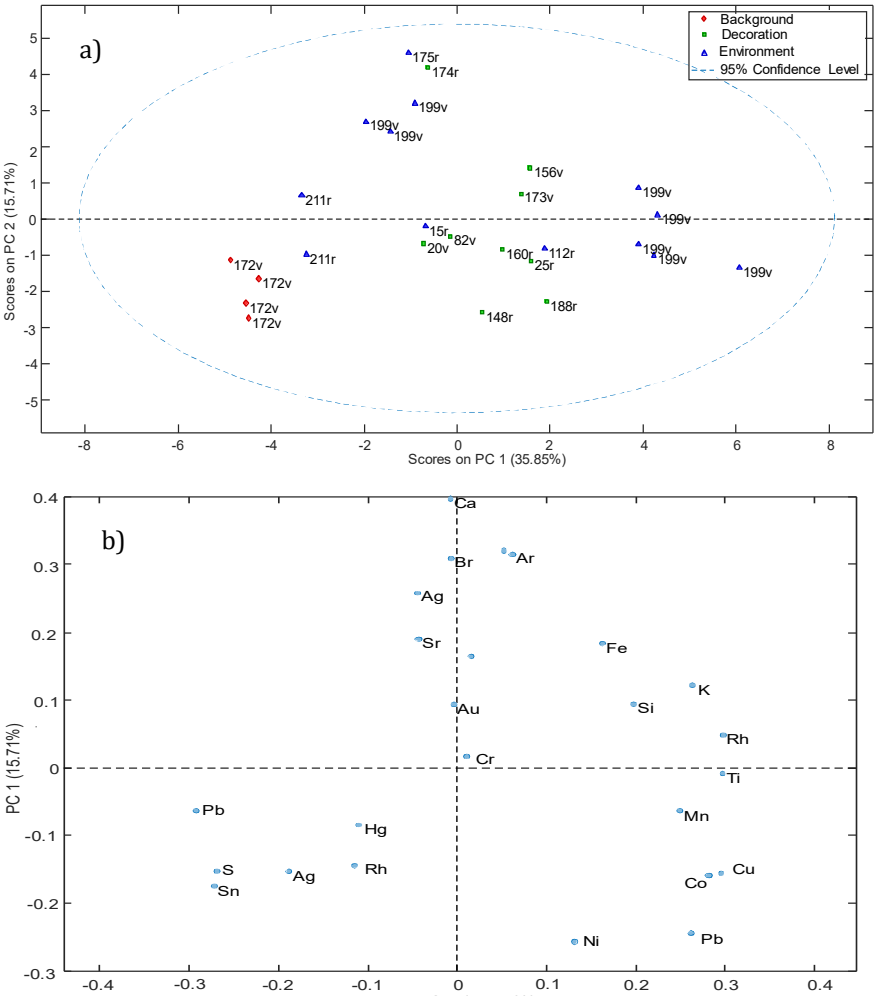


Figure 24. (a) Map of scores and (b) Map of loadings of green.

In this pigmentation, first of all we observe the separation of page 199v in two groups, which implies the existence of two green techniques in this page. The PC1 is given by the presence of copper, copper majority in a part of the page 199v, the great majority of the measured decorations, the 15r and the 112r. On the other hand, the blues at the background and on page 211r have the least presence of Cu. As for PC2, the important weight is calcium, majority in the other part of 199v, 174r and 175r.

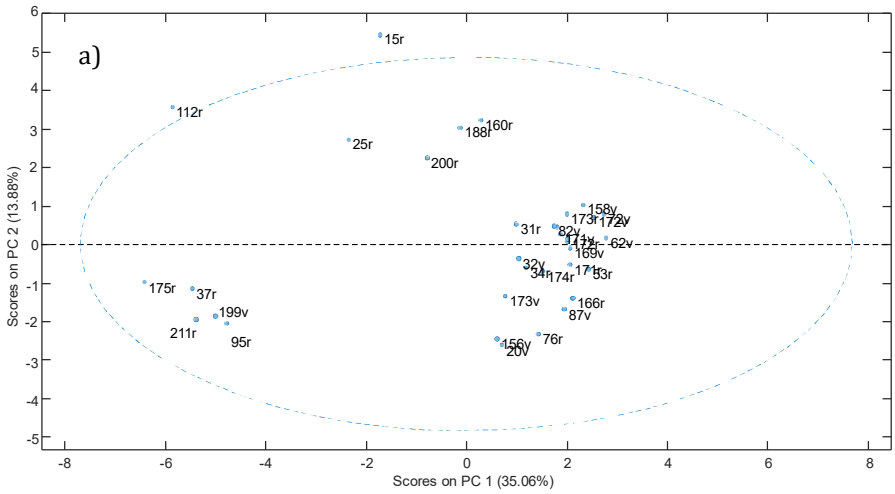
6.5.4.4. Pink

For this pigmentation, no element that could be related to the red pigmentation (Fe, Pb or Hg) was obtained, which suggests that it is an organic pigmentation. As explained in section 3.4.1., XRF is not suitable for this type of compounds, so no differences between the measurements were observed.

6.5.5. Formalism

To finish the exploratory study with individual data, the PCA is carried out on the formal categories. In this case, the matrix will be slightly different from the previous one, here the matrix is composed by 36 samples, one per decorated page, and each sample has 27 variables, explained in section 6.2, where all the variables have been represented with 0 and 1 according to the absence or presence of them. In this case PC1 represents 35.06% of the system and PC2 represents 13.88% of the system. Here the scores will also represent the pages, but the loadings will indicate each of the 27 formal variables..

We can observe the presence of three groupings through the formalism, a grouping integrated by a majority number of samples, located near the central area of the PCA. A second group composed of 6 measures (although only 5 are visible in the PCA, due to the low number of data possibilities, because everything is represented with 0 and 1, page 37v and 13r coincide in data and only one is shown). And a third group comprising 5 measures. In addition to the groupings, there are 2 pages that are not grouped with any of the previous ones, these being 15r and 112r (see Figure 25).



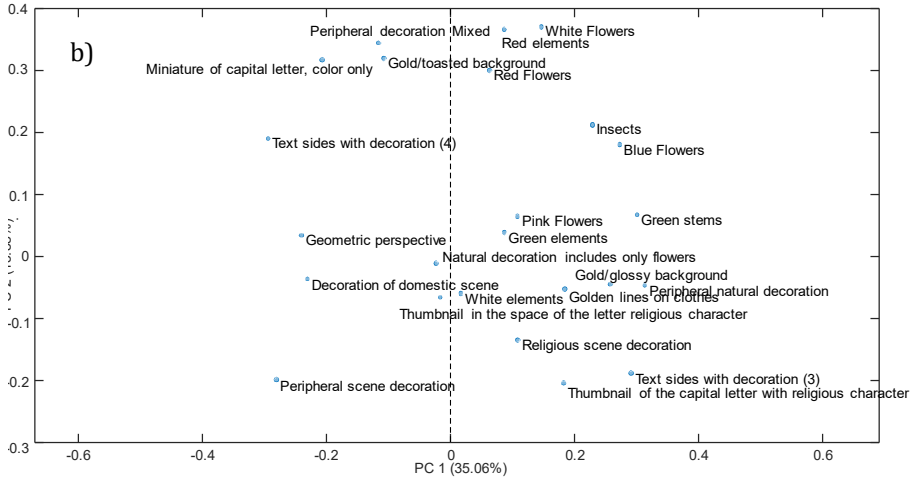


Figure 25. (a) Map of scores and (b) Map of loadings of formalism.

It is more difficult to interpret these clusters in the case of formal variables than in the case of compositional ones. In general, it can be observed that for PC1 the type of decoration is relevant and for positive loadings decorations with nature scenes appear, while domestic scenes appear in the area of negative values. Thus, PC1 would group according to these two large groups of decorations, including the majority of elements related to nature.

In PC2, the contribution of the domestic scene or one related to an scene in which characters appear in daily activities seems relevant. The cluster with negative score values would clearly appear to be of this type, including page 199v with the representation of the flagellation and page 211r, a decoration of limited quality, both different from the previous ones. For the group with positive score values, the fact that they were mixed decorations (nature and domestic 112r and 15r) would contribute. For the rest of the miniatures, located in this area, it could be relevant that they are decorations with nature scenes that occupy the 4 sides of the text, the 25r being also a mixed decoration.

7. CONCLUSIONS

First of all, once the measurement conditions were established, it was possible to establish the procedure for the elaboration of the parchment. In addition, a low level of homogeneity was observed between the pages, as well as throughout the manuscript, although it increased over the years, a fact that was determined thanks to page 199v.Once the procedure for the support was established, we moved on to the miniatures, where we were able to observe various details. With regard to the gilding, three different techniques could be established: the capital letter, the miniatures and the backgrounds, noting that two pages (15v and 112r) did not have the same characteristics as the others.

As for the colours, it was possible to determine that different techniques were used for the same pigmentation. In the case of red, four variants of this colour have been established, with two samples (62v and 95r) that are not assigned to any specific area. As for the blues, we have found three main groups, one for folio 199v, another for the miniatures and a general one for the rest of the measures, plus a folio 211r which does not coincide with any group. The last colour analysed, from which important information can be extracted, is green. Here we can see the grouping of the background area and how folio 211r, in turn, does not relate to any grouping. Most striking, however, is the separation of the measurements on page 199v into two groups, suggesting that, at the time of its production, the same artist was already using several pigmentations.

Another important part of this project was the application of formalism to the manuscript. Here we can see how the pages have been grouped into four groups according to their formal categories.

If we want to continue with this study, the next step would be to analyse all the information together, to see if in this way, the formalism groupings are related to the pigments of the decorations.

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9. ACRONYMS

CL: Capital letter

PCA: Principal Component Analysis

MS.1859: Liber Horarum 1859

XRF: X-Ray Fluorescence Spectroscopy