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Assessment of a best practise approach for the attribution and authentication of paintings

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Table of contents

Abstract

Traditionally, authenticity has always been related to aesthetic criteria and the experts define it based on their judgements, while attribution is based on assumptions and involves a degree of uncertainty. The ever growing interest in scientific techniques able to characterise the materials and rediscover the steps behind the execution of a painting makes them widely accepted in its investigation, as they provide solid pieces of evidence.

This research discusses issues emerging from attribution and authentication studies and proposes best practise for the characterisation of materials and techniques, favouring the contextualisation of the results in an integrated approach; the work aims to systematically classify paintings in categories that aid the examination of objects.

A first grouping of paintings is based on the information initially available on them, identifying four categories: a) paintings with a strong and confident attribution, therefore considered authentic, b) paintings with documentation or markings, c) paintings with an attribution and d) paintings of which no kind of information is available.

A focus of this study is the examination of case studies, spanning from the 16th to the 20th century, to evaluate and validate different protocols associated to each category, to show problems arising from paintings and explain advantages and limits of the approach. Although there is no single approach or exclusive set of instruments to be used, the research methodology incorporates a combined set of scientific techniques (non-invasive, such as multispectral imaging and XRF, micro-invasive - using samples, such as optical microscopy, SEM-EDS, FTIR, Raman microscopy and in one case radiocarbon dating) to answer the questions and, if necessary for the classification, exhaustively characterise the materials of the paintings, as the creation and contribution of shared technical databases related to various artists and their evolution over time is an objective tool that benefits this kind of study.

The reliability of a close collaboration among different professionals is an essential aspect of this research to comprehensively study a painting, as the integration of stylistic, documentary and provenance studies corroborates the scientific findings and helps in the successful contextualisation of the results and the reconstruction of the history of the object.

Chapter 1

Literature review

1 Literature review

1.1 Introduction

The final appearance of a painting originates from a complex three-dimensional structure made of several overlaid layers able to produce a specific optical effect. Each structural layer is essential not only for the final effect, but also for the long-term stability of the entire structure. This build-up consists of heterogeneous materials (both organic and inorganic, natural and synthetic), related to the availability of materials in a specific time and place and the technique of an artist. The interactions between the different components, along with the ageing phenomena and restoration interventions over time also, play a key role in how a painting looks in the present. The investigation of a paint structure has several issues: the layers have a reduced thickness, usually 1-40 μm for pictorial layers and 100-300 μm for the grounds, and they often contain a mixture of various compounds that varies accordingly to the function of the layer.

Technical research is a constantly evolving process used to thoroughly understand the composition and the complex layered structure by means of scientific analyses, it is able to characterise the materials and understand the techniques used by the artists for the execution of their artworks, allowing comprehension of the on-going changes over time, as damages, degradation phenomena of the materials and alterations due to the artist, or by a later hand. An exhaustive knowledge of the nature and conditions of the constituent materials is therefore essential to identify specific traits related to an artist or his workshop and for the selection of a suitable and effective approach to adopt for conservation treatments, restoration measures and authentication/attribution studies.

The notion of authentication is summarised as a “culturally contingent quality associated with a heritage place, practice, or object that conveys cultural value; is recognized as a meaningful expression of an evolving cultural tradition; and/or evokes among individuals the social and emotional resonance of group identity” (Nara +20 Document, 2014). Cultural value is expressed as a series of sources of information – or facts – that should be credible and truthful to build a solid basis for authentication. As recently stated [1], authentication is not inherent to an object, but has a meaning only when associated to a statement, which concerns the nature of an object and it should be divided in sub-statements, or claims, that are then tested in order to check their reliability.

Although respect of all cultural and heritage diversity is affirmed as essential since the 1994 Nara Document of Authenticity, cultural values change according to the cultural context and constantly evolve over time, therefore fixed criteria cannot judge authenticity and periodic reviews of its determination and of the identification of values are required.

Due to the globalisation of the last years, the social and emotional resonance of cultural heritage is no longer experienced by a single community but can be significant to a broader range of communities. Although the Nara Document refers to tangible and intangible expressions, in this research only tangible objects, specifically panel paintings and paintings on canvas, will be considered.

Traditionally, authenticity has been related only to aesthetic criteria, and the connoisseurship specified an individual process made by an expert able to define an artwork's authorship. Although it is conceived as a "universal value" and an "essential driving force" [2], ICOM (International Council of Museums) states that authentication is a matter of opinion[1], thus is not uncommon for experts to disagree on the authenticity of an artwork.

Attribution, on the other hand, can be expressed as the assessment of who was responsible for creating a particular work[2]. As it is based on assumptions made by qualified experts, it involves a degree of uncertainty [3], and it should be corroborated by other sources of information. Art-historical documentation, stylistic knowledge and scientific analyses are what ICOM requires to obtain a "consensus of evidence", and thus prove the authenticity of an object. It should be taken into consideration that extensive documentation of the provenance is, for instance, very rare and easily forged, and human expertise can be biased. Nowadays, the requirement of scientific techniques is widely accepted to indisputably state the unauthenticity of a painting, while the possibility to prove authenticity remains an unexplored field.

1.2 Scientific research for the characterisation of materials

The growing interest in scientific techniques able to rediscover the steps related to the execution of a work of art has highlighted the need for a deeper understanding of the artworks and a broader interpretation, based on the combination of the art experts and valid evidence supported by scientific results. Scientific analyses for the characterisation of materials, in continuous development in recent years, provide as objective data as possible. However, only by combining the results with historical and documentary information may the object be placed within the context of its time. A considerable number of studies have reported the importance of scientific techniques, which are increasingly recognised as a fundamental component in the authentication process.

At the beginning of the 20th century, Edwards Forbes proposed a first methodology for the study of paintings, a sort of toolkit, consisting of five phases: general examination of the work, detailed observation of the surface, analysis of the materials, technical examination and comparison with

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[1] https://www.obs-traffic.museum/authentication (accessed July 2019).

[2] https://www.nationalgallery.org.uk/paintings/glossary/attribution (accessed July 2019).

historical documents to collect information on the materials used by the artist. Besides this process, there should be what the philosopher Popper proposes as a specific test of authenticity, a criterion that helps in deciding whether an object is authentic or not [4]. The theory is that no quantity of positive evidence can confirm a scientific theory, but a single negative instance is enough to reject it.

The first serious discussions on this topic emerged at the end of the 1940s, when Otto Kurz published the book "*Fakes: a handbook for collectors and students*" [5], in which he stated that scientific analyses play an extremely important role in the recognition of fakes, although they are subordinated to judgment based on the experience of the art historian. The author describes the use of microchemical analyses on pigments, X-ray radiography and photography under UV radiation. He then proposes to pay particular attention to the study of *craquelure*, which can be falsified in various ways, to the position of damages, which in fake objects never affect the faces of the figures, and to the presence of past restorations, which can certify a certain degree of authenticity. The analyses, in his opinion, are more useful in the discovery of a forgery rather than in the authentication process. Fleming is of a similar opinion, when in the 1970s he wrote about the application of scientific techniques for the detection of forgeries, providing examples on paintings, ceramics and metals [6].

In more recent times, Craddock [7, 8] proposes three different approaches for the authentication of cultural heritage, based on dating techniques (radiocarbon dating, thermoluminescence and dendrochronology), on the scientific study of composition and assembling methods (to assess the compatibility of materials with the suggested period of attribution), and on the evidence of aging of the superficial patina. Similarly, Adriaens [9] lists a series of techniques applicable to different types of materials, which in the case of paintings can be, in a non-exhaustive list, optical microscopy, X-ray fluorescence spectroscopy (XRF), Particle Induced X-ray Emission (PIXE), Raman and Infrared spectroscopy, secondary ion mass spectrometry (SIMS) and synchrotron radiation, wishing that, in the future, the multidisciplinary approach will be strengthened so as to develop methods to maximize the information coming from micro-samples. The importance of the necessary synergy between art historian, curator and scientist, necessary for authentication purposes, has been recently highlighted by Ragai [10], who also divides the technical analysis into three parts: the examination of the surface of the work, the analysis of the background, or underpainting, and a thorough study of the materials using a wide range of techniques currently available for this purpose. According to the author, the role of the scientist is to discover the fatal errors committed by the counterfeiters to identify fakes.

What is noticeable from all these studies is that, even though multi-disciplinary research is crucial to comprehend the real nature of an object, scientific techniques are in some way subordinated to art-historical studies, acting more as an objective tool able to support the ideas of a connoisseur. Another important point is the difficulty for a scientific investigation to attribute a painting, in fact its only purpose seems the identification of a fake.

However, the book "Jobarde, a rediscovered painting by Eduard Manet" [11] deals with the problem of authenticating a painting in a fairly rigorous and multidisciplinary way. The aim was not to confirm or refute the authenticity of the artwork but to weigh various aspects – the pieces of evidence – and provide a first complete methodology to be used in this field. The author focuses mainly on three aspects, and how they should be integrated: the historical and artistic study and the investigation of the provenance, the analysis of the pictorial material (based on pictology[3]) and the identification of the materials constituting the object. These three groups (historical-artistic research, pictorial technique and materials research) are each divided into sub-groups to which a positive, negative or neutral value is associated, which in turn owns a level of complexity, from low to very high, linked to how authenticity can be manipulated (for instance, written sources can show a low level of complexity, as they can be easily forged, whilst pictorial analysis is highly complex to manipulate). Scientific analyses comprehend non-invasive techniques (multispectral imaging, XRF), which were correlated to the artist's handwriting, and micro-destructive ones (Scanning Electron Microscopy coupled with Energy Dispersive X-ray Analysis (SEM-EDS), Polarised Light Microscopy (PLM), X-ray diffraction (XRD), Gas Chromatography Mass Spectrometry (GC-MS), lead isotopes). In conclusion, the interpretation of the results presents an innovative modality in the field of paintings authentication, by using the Bayes statistical model, already in use in forensic research. In a simplified way, the model deals with the possibility that a defendant is guilty or not, or in this case that a painting is authentic or fake, based on a combination of factors or evidence. In the end, the decision is made based on how high or low this probability is.

Despite this impressive multi-disciplinary study and first assessment of a methodology, this approach lacks a good definition of scientific techniques related to the aim of the project, which is not the authentication of the painting but the evaluation of an integrated approach, and therefore the use or lack of some techniques could be argued. Moreover, even though the Bayes model could

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[3] The pictology method was described by van Dantzig in 1973. According to the theory, each artist's way of painting is a combination of variable and invariable elements. The invariable ones are found in every work, because they are produced unconsciously by the hand of the artist and in combination with the tools used (brushes, spatulas, etc.). The variable elements, on the contrary, are intended changes of direction of the pictorial lines, depending on the fact that the object being painted is chosen consciously by the artist and is different from what has already been painted in other works. Furthermore, the concept of spontaneity foresees that spontaneously painted lines cannot be imitated, and therefore falsified.

afford a solution, the weights of each piece of evidence and the final probability are measured by a subjective interpretation.

1.3 Scientific research on case studies: the state of the art

In terms of scientific studies, there is a general lack of published research on case studies, therefore very few studies concern the investigation of materials and paint technique of a specific artist.

Based on published literature, two general groups may be identified. In the first, scientific analyses exhibit the powerful ability to detect fakes and forgeries, propose a date of undated objects, and confirm or disprove the attribution of disputed/lost paintings, based on the identification of specific materials with a characteristic date of commercialisation. The second group consists of well-known paintings, which are considered to be authentic. The meaning of scientific analyses, in this case, is to show the potentiality and the degree of information that can be collected using various protocols or to characterise the palette of specific artists, possibly over time.

A representative selection of the first group of papers and their main issues are addressed below.

1.3.1 Scientific research confirming or disproving the attribution

1.3.1.1 Identification of fakes and forgeries

The identification of fakes and forgeries is the first and easier application of scientific techniques, because one single piece of evidence not compatible with the attributed time or suggested artist classifies the object as inauthentic.

An interesting case, although concerning a material other than paintings, emerged from the study of a confiscated parchment manuscript [12]. Archaeometric analysis (transmitted light, UV radiation, XRF) dated the object to the Middle Ages, but the graphological examination of the writings and in particular radiocarbon dating analysis showed a much more recent date, at least after the Second World War. The biological analyses finally indicated that the manuscript was intentionally buried to accelerate the deterioration, proving a likelihood of fraud. The importance of the scientific analysis, in particular radiocarbon dating, proved that the object was a fake. A similar approach may be carried out for paintings, selecting a different set of techniques able to characterise the complexity of mixtures.

Establishing the dates of commercialisation of pigments and binders is of utter importance and easily allows the discovery of anachronisms: a specific year acts as *terminus post quem*, so as a cut-off point as to when an artwork could have been made, if an anachronistic compound is found a fake or forgery is identified. For instance, the studies carried out on paintings attributed to Ljubov

Popova [13], Natalia Goncharova [14] and Jackson Pollock [15] tend to reinforce the belief of the importance of materials characterisation and, above all, the knowledge of the dates of commercialisation of pigments and binders, in order to support stylistic and provenance studies. The anachronisms recognised in these paintings allowed their identification as fakes.

However, even the negative evidence needs to be treated carefully. A painting attributed to Marc Chagall [16] was examined to verify 1910 as the suggested date of execution. The analysis showed that, due to the presence of phthalocyanine pigments, the painting could not have been created before circa 1938, when these compounds were widely commercialised. Though, the lack of a protocol or information about previous analyses failed to give information about possible retouched spots where the analysis could have been made, therefore altering the date of the painting. In any case a later date did not exclude that the painting was made by the same artist, Marc Chagall (1887-1985), but at a different time to the one proposed initially; historical and stylistic information is required to solve this kind of doubt, to define if the style of the painting fits with any other stylistic period of the artist.

Surprisingly, although several analyses were carried out on modern/contemporary paintings, so far, to the best of my knowledge, no published example was found for the investigation of ancient ones.

Another issue exhibited by this approach is that it tends to identify authentic or fake objects, without taking into account any options in between. Scientific techniques are a powerful tool for this purpose, but the problems encountered in the authentication field should be further investigated.

1.3.1.2 Chronological period for undated objects

A considerable amount of data has been published in the literature on the history of pigments over time and their date of commercialisation [17–20]. It has been demonstrated that scientific techniques are also able to propose the date of an object of which no information was available before, due to the identification of some characteristic pigments that have a documented date of commercialisation. However, there seems to be little written on this aspect. Several paintings on paper depicting Taoist priests [21] were analysed as a result of scheduled conservation treatments, which required the knowledge of pigments, technique, fibres and adhesives. The presence of some pigments, such as emerald green and synthetic ultramarine blue dated the objects to 1828, gaining new insights on these artworks, which had not been studied before. The latter pigment was also found on another painting on paper made during the mid-Qing Dynasty (17th – 20th century), which allowed dating this object to at least 1828 [22].

Together, these studies outline how this kind of approach reveals its usefulness when the painting is contemporary, while in the scenario of an ancient painting the dating based on pigments is more difficult. Until the end of the 18th century, the pigments used in art are mostly the same and were ground by the artists themselves; it was only during the Industrial Revolution that new pigments made by suppliers entered the market and could therefore be associated to a specific year of commercialisation. Finding characteristic pigments allows delimitation of a timeframe, but a possible forgery using ancient materials cannot be excluded.

1.3.1.3 Confirm attribution for disputed/lost objects

A few studies claim the ability of scientific techniques to confirm the attribution over disputed or rediscovered objects. The attribution to Vermeer of the painting *Young woman seated at a virginal* [23] was disputed over time, but the results from different techniques complemented each other and gave value to the evidence that the painting could be an original one. *Saint Praxedis*, in a similar way, was occasionally attributed to Vermeer, but a thorough stylistic study [24] and the isotope analysis on lead white, which traced the origin of lead to a northern European source [25], provided consistent evidence supporting the attribution.

For an example of a 20th century painting, *Violon. Céret* by Pablo Picasso [26] was considered a lost artwork, but the analyses on the materials of the object (especially the use of mummy brown and a triterpenic resin for the black pigments, both mentioned by Picasso in his letters from Céret) showed compatibility with the time of its suggested creation (1912), which was confirmed by the stylistic information and the study of the documentation. On this basis the authors formulated a judgement, but the absence of history related to this painting may affect its authenticity.

The case of the Malatesta painting [27] shows a result based on the compatibility of materials with the suggested period of attribution. In this case study, the presence of chrome yellow, synthetised in 1809, and of barite, need to be further investigated, especially considering that the first attribution of this painting was to Sir Thomas Lawrence, the creator of chrome yellow, and that barite is a very common material (mixed with lead white) for a typical 19th ground and was identified everywhere on the painted surface. The methodology applied in this case is not reliable, it for instance lacked a UV documentation, which could have helped to identify the alleged chrome yellow retouched areas, and missed a clear and correct historical contextualisation. Without collecting paint samples it is not possible to conclude the attribution of this artwork and only hypotheses could be made. Materials drawn from this study must be treated with a degree of circumspection.

Collectively, these case studies outline the critical role of the contextualisation of scientific results – guaranteeing the authenticity of the materials does not guarantee for certain the originality of the painting.

A remarkable example of this is provided by an attribution study of *Guitar*, a painting attributed to Picasso [28]. The object was investigated using several techniques to identify pigments and binders and find possible chronological incompatibility with the artist's artworks. The results showed that all the materials identified are widely used in art history since the beginning of the 20th century, and consistent with Picasso's lifetime (1881-1973). However, the authors did not consider this case study complete, and problems related to authentication are highlighted: the research must also be based on an art-historical investigation and a detailed study of the provenance of the object.

Given all that has been mentioned so far, one may suppose that what tends to reinforce the belief that the artworks are authentic is the successful combination of several techniques, offering a more comprehensive study of the object and reaching results that can be integrated to collect information that exhaustively characterise a painting.

In this way, compatibility with a period or an artist's lifetime is assessed. An essential step further is the comparison of these results with other objects unanimously attributed to the same artist as the object under study. This offers the only way to assess if the outcomes from a specific painting fit into an artist's technique. All the case studies described previously were carried out without comparison with a materials' database of the specific artist and therefore the final authentication is never reached.

Moreover, as shown in Table 1.1, the combined set of techniques used for each case study varies considerably. Finally, the integration with other sources, such as stylistic studies and research of the provenance should be strongly advised.

1.3.2 Scientific research for authentic paintings

As previously stated, the second grouping refers to paintings exhibiting an attribution based on solid sources, therefore considered "authentic" by a large number of experts, that are then studied using several scientific techniques to characterise the palette of an artist and, to a lesser extent, the technical evolution over time. This knowledge would support all the studies of attribution and authentication. However, techniques vary according to the case studies possibly due to their availability, and scientific research is rarely integrated with historical and artistic information.

Specifically, research on paintings with a confident attribution to a certain artist are limited, sometimes relating only to a very specific period of the artist's lifetime. In particular, there is a general lack of research on paintings made before the 19th century.

Only a few case studies concern artworks made in Europe in ancient times. A study [29] focuses on the use of oil binder and pigments in the workshop of the Master of the Vyšší Brod Cycle, the most important painter in the period around the 1340s in Bohemia, investigating the painting technique in

Central Europe in the 14th century. The palette and painting techniques of Jorge Afonso (c. 1470–1540), a 16th century Master of the Lisbon painting workshop, was characterised based on a set of 14 paintings from the most significant altarpiece assigned to this artist and his workshop [30]. Paintings by Lorenzo Lotto (1480-1556/57) between 1505 and 1556, with a narrowed focus on the 1508-22 period, were studied to investigate the technical evolution of this artist over time [31]. The artworks made by Leonardo da Vinci (1452-1519) were mostly examined using non-invasive analyses and to study the *sfumato* technique [32–35]; only the *Virgin of the Rocks* of the National Gallery of London was sampled and deeply characterised thanks to a scheduled restoration [36].

In terms of modern and contemporary paintings, a number of studies were published on different artists, included but not limited to the following examples.

Several isolated case studies are investigated using different techniques, such as a canvas painting by the Serbian artist Milo Milunović [37] and the *Portrait de Suzanne Bambridge* by Paul Gauguin, analysed due to a scheduled restoration project [38].

If more paintings are investigated in the same research, the same set of techniques may be applied to different objects, allowing the comparison of the results as well as the extensive examination of the palette of the artist. Two paintings made by Francis Picabia in his late period [39], a series of artworks belonging to the *Olii* by Lucio Fontana [40], twelve paintings by José Veloso Salgado [41], several paintings by Pousão [42] provide examples of a more thorough investigation of the palette of an artist.

Several studies made by different research groups may be carried out if the artist is well-known. For instance, *Number 1A* (1948) [43] and *Alchemy* (1947) [44, 45] by Jackson Pollock (1912-1956) were investigated using non-invasive and micro-invasive techniques. Vincent Van Gogh's (1853-1890) artworks were studied in a limited way, with a particular focus on the white paint impasto [46] or on the degradation of chrome yellow in the wide-world famous *Sunflowers* [47].

Edvard Munch (1863-1944) and Pablo Picasso's published literature are two examples that are currently examined but systematically explored in further chapters.

Edvard Munch is globally acknowledged as one of the most prolific artists in the Twentieth Century and almost 1700 artworks are included in his catalogue [48]. Following an evaluation of the published art technical studies, some pigments were distinguished based on the period – from 1890s to 1927-29 [48–54]. One of the major drawbacks of this approach is that each painting was studied by a different set of analysis, therefore the results are not complete. For instance, some paintings were investigated using SEM-EDS and lead and chromium were identified, suggesting the presence of a lead chromate. In other cases, when Raman microscopy was used, chrome yellow was univocally identified. Moreover, the purpose of some studies did not provide scientific analyses on every colour, therefore the palette is not fully reconstructed.

The artist most widely investigated is probably Pablo Picasso, as his long life and prolific artistic career allowed him to use several materials and styles. Even though Picasso created a great number of paintings during his long lifetime, only a few high-quality studies are published [26, 55–63]. These studies describe pigments and binders identified on paintings spanning from the end of the 19th century to 1946. It should be taken into account that Picasso went through a ceaseless evolution through his lifetime and experiences different phases in his style, at the moment not yet investigated from a material point of view.

A few issues emerged from this analysis. Occasionally, an artist's palette has been investigated by only a case study; if more paintings were analysed, the results published in literature can be scattered in several papers and related to different timeframes. Finally, the techniques used are not often the same for each painting analysed: the results are therefore not comparable and sometimes not exhaustive. What is noticeable is how difficult is to have access to an exhaustive and methodical database related to each artist. A few examples are available online, such as the non-invasive analyses database of paintings of the Scuola Normale Superiore of Pisa[4] and the On-line Picasso Project[5], which mostly contains art historical information and that of provenience.

The study of a Van Dyck painting [64] with a disputed attribution moved in the direction of the necessitation of a comprehensive database. The authors propose a two-step procedure, starting with the definition of an artist's fingerprint, based on already published literature, and then the characterisation of the object under study by employing several techniques, to match them in the fingerprint assessment. Further technical studies on van Dyck's artworks seem necessary to increase the knowledge of his *corpus* of artworks, but overall the authors provided important insights into van Dyck's early period (1613-21).

Towards this aim, an in-depth project on Francis Bacon's artworks aid the authentication issues [65, 66]. The analysis of a consistent number of paintings with a wide range of techniques (GC-MS), SEM-EDS, PLM, Fourier Transform Infrared Spectroscopy (FTIR) and Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS)) coupled with the materials found in the artist's studio was the basis for a first attempt of a technical database, created also with the aim of providing help in authentication issues, particularly with regard to current forgeries of Bacon's artworks.

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[4] http://www.artivisive.sns.it/dipinti/homepage.html (accessed September 2019).

[5] https://picasso.shsu.edu/ (accessed September 2019).

1.4 Discussion and remarks

To conclude this chapter several aspects can be taken into consideration. Firstly, a combination of several techniques should be proposed to exhaustively characterise an object, as sometimes the information is only partial. The set of techniques should be chosen based on the question to be answered, therefore different protocols could be proposed. Moreover, an integrated approach between scientific analyses and art-historical and stylistic studies appears essential to contextualise the results. Techniques should not be considered subordinate to other kinds of information: they provide legitimate support to the other sources of information and therefore corroborate the results. In this view, the facts constituting the cultural value of an object, as assessed by the Nara Document mentioned at the beginning, can rely on verifiable and more standardised sources.

Moreover, between what is original and what is entirely fake there are a series of intermediate objects, often not taken into consideration but that need special consideration. The identification of the essence of the artwork can help to understand its value and the reasons behind its creation in a particular historical context.

Finally, two wide groups of artworks were considered in published literature: the category where scientific analysis may help in confirming or disproving attribution (uncovering contradictory evidence on a painting, proposing a date range and solving issues related to disputed/lost paintings), and the one in which authentic artworks are studied to gather new information on an artist’s palette and working methods. Although questioning the degree of reliability of the results is a critical evaluation of the study, the essential further step for the undoubted identification of an original is the comparison of the outcomes with published data; therefore sharing the results on case studies and creating databases for each artist is fundamental for this kind of research. It is important to remark that documentary research, stylistic evaluation, the study of the provenance are only some of the other fundamental aspects that should always be integrated into the investigation of a cultural object.

The globalisation phenomenon and the consequent sharing of cultural values among several communities may also reinforce the importance of this aspect, and as suggested by the Nara Document in 1994, even though a unique and standardised protocol is not affordable, given the heritage diversity, analytical processes to determine the authenticity respectfully for all cultures are encouraged, especially in a multidisciplinary consensus able to understand values of each culture and preserve cultural heritage for the future.

1.5 Scope of the thesis

This research is primarily aimed at the identification of best practises to understand the nature of a painting, improving the approaches for the characterisation of materials and techniques and demonstrating the importance of the reconstruction of the history of the object. The thesis aims to contribute to new insights into the complex field of attribution and authentication studies, providing a first differentiation of paintings based on the information available on them and suggesting a classification into categories.

A focus of this study is the examination of case studies in order to evaluate and validate different protocols, showing problems arising from real cases, spanning from the 16th to the 20th century, and proposing possible solutions. The research methodology incorporates a combined set of scientific techniques able to exhaustively characterise the materials of the paintings, bearing in mind that there is no single approach or specific and unique set of instruments to be used. What appears essential is the integration of stylistic, documentary and provenance studies, as the reliable collaboration with other professionals corroborates the findings and thus helps in the successful contextualisation of the results.

The overall structure of this dissertation takes the form of six chapters. Following the introductory literature review of Chapter 1, the sections of Chapter 2 will examine an assessment of the terminology to use between what is entirely original and what is fake, attempting a proposal of classification, and the experimental methods applied for the case studies of the work.
Artworks can then be differentiated in four categories: a) paintings with a strong and confident attribution, therefore considered authentic, b) paintings with a sort of documentation or markings, c) paintings with an attribution and d) paintings of which no kind of information is available.
Each one of these categories is treated separately and the detailed investigation of case studies is reported in order to describe the problems encountered and propose a set of techniques able to solve them.
Chapter 3 deals with artworks that have a confident attribution to an artist, made by an art expert and based on a strong art historical research and/or study of the provenance. Two best practises are proposed, based on a non-invasive set of techniques for objects where sampling is not allowed and a micro-invasive one if samples are available.

The paintings taken into consideration in Chapter 4 show documentation, namely inscriptions on the back, signatures of the artist, markings and seals, archival documentation and so on. The assessment of the authenticity of the different kinds of documentation is the first step to undertake, so to define if it is contemporary to the painting, thus corroborating the attribution, or not, and in that case, determine if it is a misattribution or a fraudulent action.

Chapter 5 includes paintings with an attribution; usually, this is not based on strong evidence and not proposed by an art expert, and therefore it needs to be carefully validated. Based on the detailed study that one wants to achieve, following the main question to answer, the level of characterisation starts with the evaluation of the chronological period, possibly the geographical context, and finally of an artist. Moreover, normally paintings have a single attribution (to a timeframe and/or an artist), but sometimes in a more complex situation, they can show multiple attributions over time, both related to diverse timeframes or artists.

Chapter 6 considers paintings of which no information is available, thus indicated as unknown paintings. In this case, the establishment of a best practise should be able to find a period, possibly a geographical setting and ideally an artist. The object can then be classified in one of the categories found by the terminology of Chapter 2.1.

Finally, the conclusive remarks give a summary and critique of the findings, tying up the various strands to propose a series of approaches to be applied depending on the type of object under study. Areas for further research are also identified.

Disclaimer: any attribution/authentication of works analysed in this dissertation is solely by the dissertation's author, and has not yet been endorsed by the Institution to which the objects belong.

Table 1.1. Published studies related to attribution/authentication issues. For each paper the techniques applied are indicated.

		NON-INVASIVE							MICRO-DESTRUCTIVE (the sample is not destructed)			MICRO-DESTRUCTIVE (the sample is destructed)			
		Multispectral imaging				Superficial analysis			Cross-sections or samples						
		UV	vis	IRR	X rad	XRF	Raman	FTIR	SEM-EDS	FTIR	Raman	GC-MS	Py-GC-MS	^{14}C	Other
Published scientific papers	Al-Bashaireh *et al.*, 2017	✓				✓								✓	
	Chaplin *et al.*, 2014						✓	✓							
	Saverwyns, 2010	✓									✓				
	Khandekar *et al.*, 2010								✓	✓	✓	✓	✓	✓	LDI-MS
	Chaplin and Clark, 2016						✓								
	Edwards *et al.*, 2015										✓				
	Burgio *et al.*, 2005			✓	✓		✓b)		✓						Stereo, PLM, chemical test
	Stella *et al.*, 2018	✓	✓	✓				✓	✓	✓		✓	✓		FORS HPLC
	López-Ramírez *et al.*, 2015								✓	✓	✓	✓			OM
	Li *et al.*, 2017					✓		✓							XRD
	Harth *et al.*, 2017			✓	✓	✓a)			✓c)						
	Russell *et al.*, 2012								✓	✓		✓	✓		PLM
	Zheng-feng Liu *et al.*, 2019					✓	✓								3D video-microsocpy

a) Scanning macro-XRF; b) FT-Raman; c) FE-SEM.

Acronyms

^{14}C	Carbon-14 (radiocarbon)
ATR	Attenuated total reflection
BSE	Backscattered electrons
FE-SEM	Field emission-SEM
FORS	Fiber Optics Reflectance Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
FT-Raman	Fourier Transform Raman Spectroscopy
GC-MS	Gas chromatography–mass spectrometry
HPLC	High Performance Liquid Chromatography
IRR	Infrared Reflectography
LDI-MS	Laser desorption ionization mass spectrometry
MA-XRF	Macro - XRF
OM	Optical microscopy
PLM	Polarized light microscopy
Py-GC-MS	Pyrolysis–gas chromatography–mass spectrometry
SEM-EDS	Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Analysis
UV	Ultraviolet
VIS	Visible light
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy

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Chapter 2

Materials and methods

2 Materials and methods

2.1 Overview of the terminology

Among what is entirely authentic and what is fake there are various intermediate hybrid forms that require careful evaluation, as firstly proposed by R.H. Marijnissen in 1985 [1], which can be divided in original paintings, replicas, copies and fakes. Taking into account that each group contains different sub-groups and that sometimes it is difficult for an artwork to fall into a single category, an attempt at proposing a thorough classification is outlined.

For an accurate classification, scientific analyses require to be coupled with art historical information and studies of provenance to overcome the challenges of this topic. Despite the complicated issues about this subject, which hints to the need of a better clarification, the overview presented here aims at providing a simple but complete guide of the sub-categories in which a painting could fall into, enabling a terminology that can be shared among different professionals of the art world.

2.1.1 Original paintings

Original artworks, signed or not, are commonly entirely painted by an artist [1]. The certainty of their originality derives from the possibility of tracing them back to the first client and thus reconstructing the provenance.

Original artworks completed with the assistance of a workshop

In the Renaissance period, for instance, a Master often completed the artworks with the assistance of a workshop. Paintings created in this way involve a close interaction between master and pupils, making it difficult to distinguish different hands [2, 3].

Original artworks resulting from a cooperation between two or more established artists

A painting could also be the result of cooperation between two or more established artists, each responsible for a part of the execution [2, 3].

2.1.2 Replicas

Replica means a copy of a painting, in its entirety or part of it, painted by the same artist of the original one or close *entourage*, with the idea of remaining faithful to the prototype [1].

Replicas made by the workshop/ Variant

A variant is based on a prototype made by a Master, modifying the basic or a single part of it, such as composition, details, colours, but always allowing a recognition from the original from which it descends [2, 4]. It is considered also a replica and it can be painted by a Master and by the workshop.

2.1.3 Copies

The terms copy and replica are often used as synonyms, but even if copies usually are paintings which clearly retrace an original prototype, they are made by different artists from the original ones and made outside a workshop [1, 4, 5]. Obviously, the distinction is more difficult if the copy/replica is contemporary with the original.

In particular, copies can replace an original artwork, for instance for conservation issues, or they can have representative purpose or play an important educational role, being painted as pedagogical device [4, 6, 7].

Study-copies

A type of copy diffused mainly in the 18-19th century is the study-copy, practised in academia and museums. The paintings of the Old Masters were used as a study material for the students, who copied all or parts of the great masterpieces. They can be easily confused as studies performed by the original artist, especially if the historical period is similar.

Free/creative copies

A famous artwork is the model of this kind of objects, which are created with a certain degree of subjectivity.

Copies of parts

Only parts of an original artwork are represented.

Copies made in the manner of another painter /by a follower

Paintings made in the manner of another painter concern works of art in which a painter try to imitate and incorporate the style of another artist. They are usually made after the lifetime of the artist of the original artwork. In the case of a follower, the copy can be painted during or later the lifetime of the original artist (the follower artist had no interactions with the original one).

Souvenir and pastiche

There are two other categories worth of discussion, namely souvenir and *pastiche*.

Souvenir is a copy of an artwork that is taken as a memory of a trip.

Pastiche is a work created assembling unrelated pieces [8], sometimes created with an ironic intention [9].

2.1.4 Fakes and forgeries

Fakes and forgeries are works that imitate a painting with the intent to deceive [6, 9–11]. The reasons can be different, such as an economic advantage or a psychological motive (personal prestige or revenge) [12], but it is always implied deception [6, 12–14].

Concerning the Italian law[6], there is a distinction within the category of fakes and forgeries related to altered, counterfeits or reproduced artworks. It should be pointed out that a painting can respond to precise legal requirements and be accepted by the law as a certified copy created without the will of fraud[7].

Altered artworks

The alteration consists in the modification of an artwork to make it look like a work of a different artist. In this case, the aim of the forger is undoubtedly reprehensible because, in addition to placing a false object on the market, it destroys at the same time an authentic one.

A deceptive element, such as an inscription on the back or a signature, can be applied to add value to the object, or artworks can be severely altered through human intervention in order to make them look like another artist's creation [1].

Counterfeiting

Counterfeiting is the creation of an artwork from scratch, according to the style, *ductus* and iconography of a known artist, with or without a signature copied from the original. If they are inspired by the style of an artist, forgers can create an artwork with a perfect technical-aesthetic and/or iconographic resemblance. These cases are more complex because they consider works as integral fakes, manufactured with modern materials or, in an even more complicated scenario, ancient ones [1].

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[6] *Codice dei beni culturali e del paesaggio*, d.l. 42, 22 January 2004, art.178.

[7] *Codice dei beni culturali e del paesaggio*, d.l. 42, 22 January 2004, art.179.

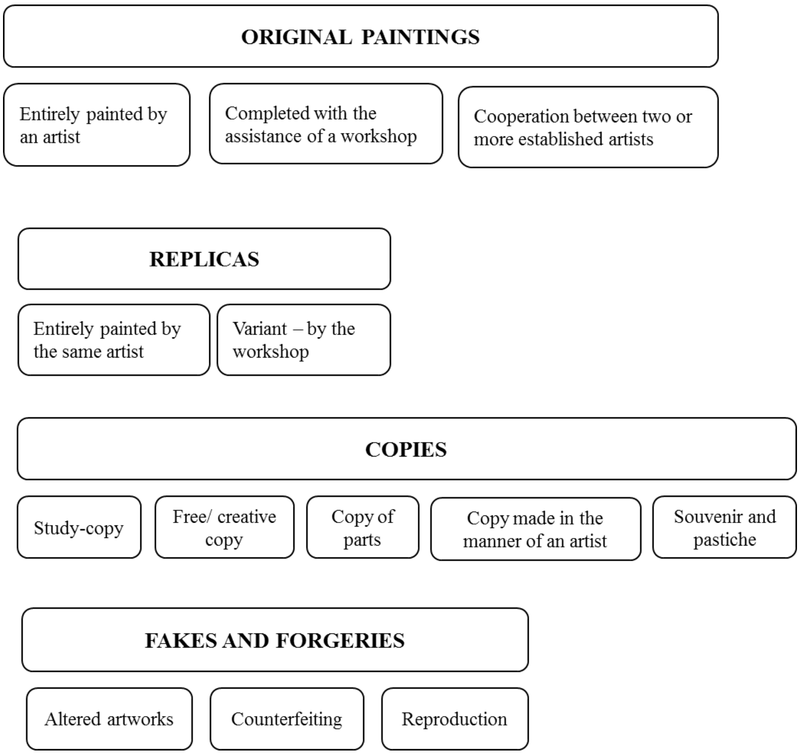
Reproduction

Reproduced artworks are made with a mechanical method, for instance by photography or print, in order to obtain, for example, bronze or plaster objects, or graphic copies.

Misattributions

The artworks described in all the previous categories can become frauds by misattribution made by an expert.

A misattribution is defined as an error made in determining the original artist of an artwork, done for honest reasons, including a restoration that has altered some fundamental clues or an object created by an artist's school, or fraudulent, in the event that an expert or group of experts has the intent to deceive for a personal illicit purpose [10].



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2.2 Experimental methods

Scientific analyses for the examination of artworks are in continuous development, providing data as objective as possible about paint materials, executive technique, state of conservation and environmental context. The use of a single technique usually cannot solve all the attribution and conservation issues, therefore the research methodology should adopt a complementary and integrated set of techniques. In addition, the complex nature of an artwork also requires a multidisciplinary approach in which a wider interpretation, comprehending the combination of scientific results with documentary, stylistic, historical, of provenance researches, is able to insert the painting within a specific context and thus interpret the history of the object.

A detailed and systematic documentation of an artwork gathers new insight into a chronological period or an artist's materials and techniques, collect useful data for future conservation treatments and also makes more difficult the illicit use of cultural object and thus the spreading of fakes and forgeries.

The investigation of the painting through a large number of analytical techniques, such as *in situ*, non-invasive and micro-destructive ones, allow the characterisation as complete as possible of the materials and paint technique.

Non-invasive techniques are applied at first, multispectral imaging is then combined with spot analyses – such as x-ray fluorescence spectroscopy (XRF) – to have an idea of the state of conservation and the used materials. A careful examination of the surface is thus essential to reduce the issues related to the heterogeneity of the paint materials and the multi-layered structure; then the second step is represented by the sampling, when possible, bearing in mind to preserve as much as possible the integrity of the painting.

Cross-sections examination allows to gather information about the number of layers, thickness, colours, predominant compounds, presence of particles along with their size, colour and identification, and UV fluorescence colour, which hints at a possible category of organic materials (lipid, protein, synthetic materials, lakes or colourants, etc.) and in a lesser extent to an inorganic one (for instance, zinc white, barium sulfate, calcium carbonate show a peculiar UV fluorescence).

The limited number of fragments is then studied by means of a large number of techniques, depending on the sought information. In this research, optical microscopy is associated with scanning electron microscopy coupled with energy-dispersive x-ray analysis (SEM-EDS), infrared (FTIR) microscopy, Raman microscopy, as well as radiocarbon dating in a few cases, with the aim of exhaustively characterise materials, techniques and state of conservation.

A brief description of each technique applied in this research is here proposed, focusing on the basics, including advantages, limitations and technical specifications.

2.2.1 Multispectral imaging

Visible and raking light

Observing a painting with visible light is the simplest method to non-invasively document, entirely or in part, the object and its state of conservation. The use of a raking light, with the light source placed at a side with a high angle in respect to the normal of the object, allows to further investigate the state of conservation (canvas deformation, assembly of the panel, thickness of paint layers) and have a first idea of the executive technique (*pentimenti*, retouchings, colour losses, engravings and decorations); the three-dimensionality of the object is emphasised and thus the morphology of the surface.

In this work, visible and raking light photography was performed with a Nikon D800 (36 Mp) camera and AF MICRO Nikkor 60 mm 1:2.8 objective and Hama UV&IR CUT filter. The light sources are Lupo Daylight with OSRAM 800W (5500°K) lamps. ISO, aperture and time depend on the case.

UV fluorescence photography

When an atom or molecule absorbs UV radiation, transitions between quantum states are stimulated and a radiation at a longer wavelength (in the visible range) is re-emitted, called UV fluorescence and generally weak in intensity [1, 2].

This technique is non-invasive, fast, simple and practical, and allows to examine the surface of the objects. Although consisting of a similar visible colour, materials may provide a different coloured fluorescence under UV radiation, thus this technique allows to differentiate or highlight diverse features on the surface, such as inhomogeneity of varnish layers and retouched areas made with non-original materials, sometimes not distinguishable in visible light. Varnishes applied at different times are also identified, as the fluorescence increases with ageing. Pigments usually do not show a UV fluorescence, except zinc white and a few others, while binders are characterised by a fluorescence. However, copper-based ad iron-based pigments make the entire layers not fluorescent, even in the presence of a binder.

This technique do not provide the characterisation of the material, only a first general idea of some compounds, but it allows to pinpoint a few features. The presence of a thick varnish also prevent the interpretation of the image. Caution should also be taken as UV radiation can be harmful for both users and paint layers, and the analysis requires dark conditions. It is a preliminary approach able to guide the sampling and document conservation interventions over time.

In this work, UV Fluorescence photography was performed by a Nikon D800 (36 Mp) equipped with an AF MICRO Nikkor 60 mm f/1:2.8 lens, with a Hama UV&IR CUT filter. The sources for UV radiation were two Mada Tec ultraviolet sources with emission at 365 nm. The images were acquired with an exposition time of 30 seconds, ISO 100 and aperture f/11.

Infrared reflectography

The use of a lamp emitting light in the visible and near infrared region allow the radiation to penetrate in depth inside the object - depending on the materials, layers' thickness and wavelength of the IR radiation - and then be reflected at the base. This emitted radiation is captured by a detector and transformed in a visible image. Materials able to absorb infrared radiation have a low scattering capacity, such as carbon black, therefore they appear black; on the other hand, materials that do not absorb infrared radiation and thus have a high scattering capacity appear white, such as gypsum or lead white. This difference in materials distribution is expressed in a grey scale [1, 3].

IR reflectography is very suitable to investigate the presence of underdrawings, especially if made of carbon black on a white surface, and possibly the transfer method of the drawing to the support (such as pouncing, squaring, use of cartoon), but also *pentimenti*, retouched areas, previous restoration interventions, signatures or markings not visible to the naked eye.

It should be taken into account that the materials and thickness of paint layers may affect the infrared reflectography, as for instance the use of infrared absorbing pigments in the paint layers may create some alterations.

The combination of an infrared and a visible image allows to obtain false colour infrared image (FCIR), in which the images corresponding to the channels sensitive to green, red and infrared spectral regions are combined as blue, green and red components on a standard RGB image [1, 4]. Therefore, the colours of a FCIR image do not resemble the real ones but contain information belonging to the infrared region, allowing to see in a visible colour what is not visible to the naked eye.

This technique can be useful to distinguish diverse compounds of similar visible colour (for instance, lapis lazuli and azurite or diverse types of red lake), if they have a different behaviour in the IR region, providing a good preliminary analysis. However, it is not able to characterise the materials, as for instance different materials have similar nuances; moreover, also concentration, purity and mixtures affect the result. Finally, infrared reflectography is a fast and practical technique, but the false colour mode requires an elaboration at a second time thus the results is not instantaneously visible.

IR reflectography is carried out by Multi Spectral Image System Nir Digi WS (Spectra Elettronica), image sensor 5mp, Nikon AF Nikkor 28-70mm 1.3.5-4.5 objective.

2.2.2 X-ray fluorescence spectroscopy (XRF)

When an x-ray radiation beam of a specific energy interacts with a material, these primary electrons are able to displace the inner shell electrons of the specimen (ionisation event) and the re-establishment of the charge balance creates a secondary x-ray radiation, emitted from the sample and characteristic of each element contained in the sample, as each will emit x-rays at characteristic energies. Fluorescence is the absorption of high energy radiation that results in re-emission of low energy one [1]. This radiation is analysed by energy dispersive x-ray spectroscopy (EDX), which is the most common XRF system, sorting thus the energies of the photons.

XRF is a non-invasive and non-destructive technique as the instrument respects the physical integrity of the object; it is a fast, versatile and widely spread multi-elemental analysis, also suitable for portable devices, that allows a large number of measurements and gathers information as a first screening of the possible pigments present in the paint layers. The instrument allows to detect only elements with $Z < 15$ (P), and it is commonly used for qualitative analysis. Pigments can be inferred and sometimes likely identified by the detection of some elements present in their formulation, but it is essential to combine XRF with molecular techniques to fully characterise the materials [1, 6–8].

The technique does not provide insights into the composition and material distribution of the individual layers, as results are affected by the type of materials, thickness, heterogeneity of the mixtures, other than the measurement conditions: acquisition time, accelerating voltage (only if it is sufficiently high (30-50 kV) the ionisation of the atoms of the specimen is allowed), probe current (influences the number of x-rays emitted from the samples and thus the intensity of the detected signal).

XRF has a limited sensitivity of low atomic numbers, and most materials analysed in paintings consist of light elements. A complex and heterogeneous layered structure cannot be determined, as well as the distribution in depth. Spectra interpretation is also complicated, as an element emits peaks at different energy and the limited resolution does not resolve peaks with nearly identical emission energies, as mixtures of pigments containing Ba-Ti, or Pb-S or Pb-As. Even the x-ray source can create interferences, as the material used as target produce its own emission lines, which may coincide or overlap with emission lines of the sample. In this case, the W-source creates problems with Hg or Zn, so if these two elements are present in small amount only the less intense peak is evaluated. Moreover, the predominant x-ray peaks in the spectrum do not necessarily indicate the major element present.

It is important to underline that this technique should be performed after UV fluorescence photography, which allows to see retouched areas on the painting and thus avoid them in order to analyse only the original parts. Pigments based on the same elements, such as green Cu-based ones, cannot be differentiated, and that is even more visible for contemporary paintings, as they are made of several pigments, even of different colour, showing the same elements, as yellow or green Cr-based or Ca-based compounds.

XRF was performed by employing an Energy Dispersive Spectrometer (EDS) EIS-XRS38 (Electronic Industry Support (E.I.S.), Rome) with tungsten (W) anode, maximum voltage 38 kV, maximum current 0.5 mA, circular spot of 3 mm diameter; the X-ray fluorescence is detected by a Peltier cooled silicon drift detector (SDD) with Zr window. The distance between sample and detector is about 5 mm and the area selected through a laser pointer. The technique can detect the chemical elements with atomic number Z higher than 13. The analyses were carried out at 30 kV, 0.2 mA and for 300 seconds.

2.2.3 Sampling criteria and cross-section preparation

The guidelines proposed by ICON[8] comprehensively describes recommendations about sampling. Collecting samples is not always necessarily essential for the results. For instance, in order to find out if a painting is compatible with a chronological attribution, sometimes non-invasive analyses are enough. Moreover, not every object can be sampled, as for small and fragile artworks (for instance miniatures), and, when possible, sampling is not ethically

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[8] ICON Heritage Science Group, Ethical Sampling Guidance, January 2019.

acceptable for main areas (face, signatures). Anyway, a best practise should be the searching of old samples, maybe collected in previous studies, so to re-use them and avoid a new sampling.

Sampling should be requested and agreed with the owner (private collectors, Institutions, Museums, etc.) and among the professionals involved in the research. If samples are needed and agreed upon, locations and number should be decided and expressed. For instance, detached areas or edges should be find appropriate before taking a sample, as sometimes these areas do not show all the pictorial layers or were retouched in the past: moreover, the sample size should also be discussed, as different analyses may require different size.

The preparation method, chosen accordingly to the question to answer, should also avoid risk to the sample, such as losing the sample if it is too small or not cleaning it with appropriate solvents before organic analyses or radiocarbon dating, and be defined if it is destructive or not, as in the last case more than one analyses can be performed on the same sample. The last thing to take into consideration is the storage of the samples, for instance samples embedded in salt (as KBr) need to be stored in a dry environment.

The choice of numbers and location of samples needs to be evaluated in each case. There are different ways to obtain a cross-section as several embedding materials are available [9, 10]. In this work, cross-sections were obtained by embedding the samples in KBr pellets (the sample is placed on top of a KBr pellet obtained with 300 mg of KBr pressed at 2 tons for 30 seconds, the powder of 300 mg of KBr is added over the sample and it is pressed at 3 tons for 120 seconds). Afterwards, the pellet is embedded in polyester resin. The sample is then dry polished with Struers Silicon Carbide Paper (120, 500, 800, 1000) and Micromesh Carbide Paper (4000, 8000, 12000), decreasing the grit size until reaching the polished cross-section [11].

The characterisation of the cross section is firstly made by the use of optical microscopy, several elemental and molecular techniques can then be carried out for a complete characterisation of the sample.

2.2.4 Optical microscopy

A system of magnifying lenses allows to view untreated objects or specifically prepared samples (stratigraphic sections and thin sections) to be observed and documented at various magnifications. Parts of the artefacts or representative samples are documented and studied at magnifications of up to about 1000x. This non-invasive technique is helpful to examine the sample and different wavelengths can be used, such as visible light and UV radiation. This helps in the documentation of the number of layers from the support to the varnish, colour, thickness, grains size (colour, size, shape, distribution) and UV fluorescence colour. In particular, UV radiation is used as a first screening to qualitatively detect the presence of organic materials (binders, varnishes, colourants and lakes) [1].

The microscope is a BX51M (Olympus, Tokyo, Japan) with a fixed ocular magnification of 10x and different objective magnification (5x, 10x, 20x, 50x). A 100W halogen projection lamp was used for visible light, while the UV source is Ushio Electric USH102D lamp. Images were acquired with Primoplus software and by a DP70 Olympus scanner directly joined to the microscope.

2.2.5 Scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM-EDS)

This elemental technique allows the observation and analysis of objects; it can be invasive if a sample is required or non-invasive in case of small-sized objects that can fit into the sample chamber. In any case, the materials should be compatible with a vacuum chamber.

The high energy electrons beam created in the electron column scans the surface of the sample and interacts with the materials, obtaining an image in shades of grey.

Back-scattered electrons (BSE) are high energy electrons emitted from the sample when elastic collisions happen and provide imaging contrast based on the elemental composition, as elements with higher Z appear brighter. Secondary electrons (SE) are low energy ones and are emitted following inelastic collisions, providing information about the surface morphology.

A dedicated detector (EDS) enables the analysis of X-ray fluorescence emitted by the sample, allowing for elemental chemical analysis with high spatial resolution.

The high resolution and great depth of field are the main advantages of the SEM, as well as the detection limit of around 0.1 wt% [1, 12, 13].

This technique should be performed on electrically conductive samples, so a conductive surface film (mostly made of carbon or gold) is often sputtered on samples to prevent charge accumulation and thermal damage. In case of further analyses, the surface can be polished again (slightly modifying the stratigraphy). Other solutions can be taken into consideration, in this work’s case studies carbon tape is applied around the stratigraphy so to decrease the charge accumulation without covering the sample surface.

One of the problems of SEM-EDS is the interpretation of the EDS spectra, as the emission of characteristic x-rays from the sample has similar problems as the ones found in XRF: this technique allows to detect all the elements (without the $Z < 15$ limitation) but the overlapping of peaks of similar energies is still an issue.

Back-scattered electron images (BSE) and EDS spectra were collected on a low-vacuum Quanta Inspect S (FEI, Hillsboro, OR, USA), equipped with a Philips New XL-30 microprobe. EDS analyses were carried out on areas and spots and conducted using an acceleration voltage of 30 kV, a tungsten filament current of 100 μA and performed at a working distance of 10 mm for 100 seconds.

2.2.6 Fourier transform infrared microscopy (FTIR)

The technique is considered non-invasive or micro-invasive, as very small samples are required (micrograms). It is a molecular technique able to provide information from organic and inorganic, natural and synthetic materials at the same time, and it is a fast and versatile instrumentation commonly applied in the heritage field [1, 14–16].

The IR range can be divided in three parts: near, mid and far infrared; in the cultural heritage field usually the mid infrared (MIR) is used (4000-400 cm^{-1}). Wavelengths are measured in wavenumbers (cm^{-1}), which are directly proportional to energy.

The source is an infrared beam that interacts with the sample and affects the vibrational energy of the molecules. The possible movements are divided in two main categories: stretching (changes in inter-atomic distance along bond axis, symmetrical or asymmetrical) and bending (changes in the angle between the bonds, defined as rocking, scissoring, wagging, twisting and in or out of plane movements). Since the vibration of a molecule is unique, it is possible to characterise the compounds, as long as a change in the dipole moment of the molecule is implied.

The obtained spectrum presents peaks corresponding to chemical bonds between the atoms in a molecule and these characteristic absorption bands are used to identify molecular components and structures. Samples are analysed without preparation or in cross-section.

In this work, attenuated total reflection (ATR) mode was used on cross-sections, even if this mode may create distortions in the shape and position of bands. The IR beam passes into an optically dense crystal with a high refractive index (diamond or germanium). The internal reflectance creates an evanescent wave that extends beyond the surface of the crystal and into the sample, which is in direct contact with the crystal. If the sample absorbs part of the IR energy, the wave is attenuated and comes back into the crystal and then to the detector, where it is measured and a spectrum is generated.

Available reference spectra databases are of utter importance in order to confront the unknown spectrum and thus identify the compounds.

When in conjunction with a microscope, spectra are measured from small areas around 10-5 µm. Analysis are carried out by single point or mapping, the latter allows to view the distribution of different chemical compounds within the sample's stratigraphy.

The technique has a good sensitivity and is able to identify constituents in multi-layered materials, such as pigments, binders, varnishes, coatings, adhesives, colorants and dyes, and also chemical changes due to ageing. However, the identification of single compounds in complex matrices is not easy, especially if the species have overlapping bands. It is also not suitable for discriminating materials with similar chemical structures, as it can identify chemical classes but not the specific species. Moreover, inorganic materials have a higher, stronger and broader IR absorption bands in comparison to organic ones, and are often present in larger quantities, this results in difficulties in identifying organic materials. The spatial resolution limit (usually 10 µm) does not allow to characterise very thin layers, as information are collected from adjacent ones as well. Embedding materials such as synthetic resins have a typical IR spectrum, so they can create interferences in the analysis; to avoid this problem, salts transparent to IR radiation have been employed, and KBr was used in the samples preparation of this research.

FTIR analyses were performed with a microscope iN^{TM}10MX Nicolet (Thermo Fisher Scientific, Waltham, MA, USA) coupled to a mercury cadmium tellurium (MCT) detector. Attenuated total reflection (ATR) investigations on cross-sections were achieved with a conical crystal germanium of 300 µm in diameter. Spectra were collected in a spectral range from 4000 to 675 cm^{-1}, with a spectral resolution of 4 cm^{-1} and 64 acquisitions. All the spectra were baseline corrected, the CO_2 was removed from the spectra and a smooth performed.

2.2.7 Raman microscopy

The technique can be considered invasive if a sample is required, or non-invasive if the object can be analysed by a portable instrument or fit directly under the microscope.

A high energy monochromatic light (such as a laser) is the source; the photons hit the molecules of the sample in the elastic and inelastic way. The latter mode creates the Raman effect, as a difference between the energy of incident beam and the one collected by the detector after the interaction with the specimen is measured. The conjunction of a spectrometer with a microscope allows to obtain spectra from particles of around 1 µm. The spectrum is typical of each molecule, making Raman analysis a powerful tool for the characterisation of compounds. The comparison with reference spectra in available databases is also of utter importance. A single point analysis can be carried out, as well as mapping, so the spatial distribution of compounds are collected on the stratigraphy.

No sample treatment is required and both organic and inorganic compounds, natural and synthetic, can ideally be identified, with due limitations. The laser source can indeed create fluorescence of some binders and organic pigments, also present in small quantities, masking their typical signal and thus complicating their identification. Moreover, usually a single laser source is not able to get good responses from all compounds, thus different lasers should be used for a complete characterisation of the object, or different analytical techniques. The excessive laser power on a spot can also cause heating and possibly burning of the area, so a careful use of this technique is mandatory [1, 17–19].

Raman spectra were collected with a Senterra Microscope (Bruker, Karlsruhe, Germany) interfaced with an Olympus microscope (20x and 50x objective lens) and equipped with a charge coupled device (CCD) detector. The analyses were carried out with a 785 nm laser, with a power up to 10 mW. The spectra were collected in the 50-2600 cm^{-1} spectral region and with a resolution of 3 cm^{-1}.

2.2.8 Radiocarbon dating

In nature three carbon isotopes exist: ^{12}C (98.89%), ^{13}C (1.11%) and ^{14}C (10^{-10}%). While the first two are stables, ^{14}C is radioactive: it tends to turn into nitrogen with a half-life of 5730 ± 40 years [20, 21]. Its production takes place in the atmosphere, and the radiocarbon thus obtained reacts with oxygen to form carbon dioxide (CO_2), which is then incorporated, directly or indirectly, into living organisms.

All living organisms are allegedly in equilibrium with the concentration of ^{14}C present in the atmosphere; when an organism dies, the radioactive decay of the isotope begins, causing a continuous decrease of the ^{14}C content in the organism's remains [20–22].

The dating technique consists first in the measurement of ^{14}C concentration in the sample. In order to do that, the different isotopes of a sample are counted thanks to the use of the accelerated mass spectrometry (AMS) technique, available since 1977. The amount of material is relatively small (0.05-0.5 mg), and the analysis is carried out in about 50 minutes [20, 21]. The value is then compared with the ^{14}C concentration in the environment, based on the fundamental law of the radioactive decay.

The result is then translated to a calibration curve, based on data collected from other direct dating methods (as dendrochronology), and the elapsed time since the object came out of the carbon cycle can be measured [20, 21, 23].

A few problems need to be taken into consideration, depending, for example, on the fact that the production of ^{14}C in the atmosphere, and therefore its concentration, varied over the centuries according to different factors, both environmental, such as fluctuations in the cosmic ray flux and decreasing of the rate of new ^{14}C formation [1], and anthropological, as the increase of ^{12}C carbon in the atmosphere since the industrial revolution [20] and the increase of ^{14}C carbon after 1955 due to nuclear tests (bomb peak) [24].

The disadvantages of radiocarbon dating are the high cost of the analysis and the presence of only a few centres specialised in this technique, although they are increasing in number. Moreover, the sample must not contain other sources of carbon (varnishes, synthetic organic materials, synthetic fibres, etc.), which can pollute the final result, therefore the use of radiocarbon dating must be well thought out and included in a series of analyses able to characterise the object from the material point of view. Despite the high precision measurements that can be obtained from an effective chemical pre-treatment and the latest technology instruments, the results of radiocarbon dating will always be in wide ranges due to fluctuations in the atmospheric content of ^{14}C [21].

The applications of radiocarbon dating mainly concern the archaeological field, the Quaternary geosciences, linked for example to climate change, the biomedical sector and the forensic one [21].

In the field of cultural heritage, the technique is mainly applied to the study of archaeological materials (wood, bones, horns and ivory) [21], textiles [20], leather, manuscript, parchments, papyri [22], but results have also been obtained from iron and, to a lesser extent, bronze materials belonging to archaeological excavations [25, 26].

The multi-layer and multi-material structure of a painting provides different sources of carbon. The dating of the support is probably the most common one, as panel or canvas are made of organic materials [27]. ^{14}C is also found in binding media (i.e. tempera, oil, resins) and some pigments, such as lead white, calcium carbonate and Prussian blue, and varnishes. Recently, the oil binder was successfully dated [28], as well as lead white [29].

Radiocarbon also provides a useful method for studying the authentication of cultural heritage (art forgery) [30]. In the case of contemporary art, for example, an innovation is provided by the study of the bomb peak: nuclear tests in the atmosphere after 1955 result in doubling the concentration of ^{14}C, reaching the peak in 1963. As tests were banned in 1963, the concentration is now decreasing, thus this is the only dating method for artworks created from 1955 to the present [20, 21, 24].

In this research, radiocarbon dating was carried out at the facility of the ETH Zurich (Switzerland), Laboratory of Ion Beam Physics. Sample treatments and analyses are expressed in Table 2.1.

Table 2.1. Scheme of the sample treatment for the radiocarbon dating at the ETH Zurich.

Treatment	**Method**	**Notes**
Photographical documentation + weight		
SOXHLET	Chloroform (60°C, 1h)	Removal of pollutants
	Hesane (55°C, 1h)	
	Acetone (60°C, 1h) + dry (30 min, 60°)	
	Ethanol (60°C, 1h)	
Photographical documentation + weight		
ABA	HCl (5ml)	- Removal of carbonates - 30-60 min in the oven, then wash with Milli-Q H_2O
	NaOH (5ml)	
	HCl (5ml)	
Dry (overnight in the oven), photographical documentation + weight		
Grafitisation	Standard: oxalic acid (known concentration of carbon, used as standard for the calibration)	- OXA e blank standards are prepared in the same amount as the sample - Sample reduced to carbon
	Blank (material without carbon)	
	Sample	
EA-AMS → dating of the sample		
Elaboration of the data and calibration with OxCal		

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Chapter 3

Authentic paintings

3 Authentic paintings

A confident attribution to an artist plays an important role in the value of a painting, and if it is based on art historical studies carried out by connoisseurs and corroborated by detailed research of the provenance, the object is normally considered authentic. However, a major drawback with this kind of approach is the subjectivity affecting the research. Scientific investigations characterise the materials of the painting and the technique of execution, as well as the condition of the object, therefore providing an objective ground for authentication studies. Collecting results from authentic artworks allows to improve or create databases on different artists. This is an essential aspect of the work because it is only by assessing the materials used by an artist, and his/her technical evolution, that is possible to create a solid base for future studies regarding the attribution of a painting with an uncertain or unknown attribution.

This chapter is divided into two sub-groups, described below, with two protocols proposed for the investigation of the objects.

In the field of cultural heritage taking samples is not always allowed due to several reasons, for instance, the fragility or the small dimension of the painting, the value, or good access to the object. In this case, only non-invasive analyses can be performed, as sampling is not considered ethically acceptable. The small dimensions of portrait miniatures (circa 5 cm x 8 cm) make these objects an excellent example for the proposal of a non-invasive scientific protocol. The art of miniature was a branch of art that started to spread in England in the 16th century and in which English artists excelled. English miniatures attributed to Isaac Oliver (c.1565-1617) and Nicholas Hilliard (1547-1619) are taken into consideration in this research. Their study has paved the way towards a serious study of early English portrait miniatures, which, until this point has been lacking.

When sampling is allowed the fragments taken from a painting and analysed in cross-section can provide additional information on the mixtures used by an artist, the number of layers and therefore the technique. The study of five paintings attributed to Gianpietrino, a pupil of Leonardo da Vinci, using micro-invasive best practise sampling helped to clarify some features of this artist, who is not only an ambiguous figure of the 16th century, as only sporadic information about his life is available, but also a sort of container for a large number of artworks erroneously attributed to him.

3.1 Non-invasive analyses – Portrait miniatures

3.1.1 Introduction

The art of the miniature[9] is characterised by the minuteness of the technique, impeccable even at a close observation, and the specific purpose of the object, usually offered as a personal gift or commissioned to demonstrate devotion to a political patron or a family member [1–3].

The first miniature painters probably arrived from Ghent and worked at the court of Henry VIII; from the 16th century the technique began to spread in England. Miniatures played a key role in both Tudor and Stuart courts and they were a strong part of British art until the 19th century, when the technique started to decline after the invention of photography. Portrait miniatures, or limnings, were considered a separate art from painting or drawing, due to their distinctive materials, technique and colour scale, as stated in Hilliard's treatise (*The art of limning*, 1598); miniatures are painted on vellum, this is then affixed to a playing card with starch glue. A number of pigments can be used and are typically mixed with gum arabic. Among the artists of the 16th century, Nicholas Hilliard (1547-1619) was the most skilled and famous miniature painter who worked at the court of Elizabeth I. Specific features, described in his treatise, characterised his style. The fine reproduction of jewels and metals in his miniatures descends from his training as a goldsmith; while to imitate the various textures of fabrics, three hues of white were used to achieve the desired final colour; finally, the flesh tones were always very pale and applied with only a few brushstrokes over a ground layer termed 'carnation' (which usually covered the whole surface of the miniature) [4].

By the 17th century, however, the opening of England towards Europe increased the demand of a more European art, characterised by a greater realism, new pictorial developments, such as the use of volume and space and aerial perspective, and the study of the human anatomy. Hilliard's technique was considered old fashioned and his fame began to decrease, while his pupil, Isaac Oliver, rose in popularity.

Oliver (c. 1565-1617) was born in Rouen and arrived in England as a refugee. He was probably already trained as an artist, because he left a series of high quality drawings that preceded his miniatures, but he learnt the art of miniatures from Hilliard. Oliver's style was different from Hilliard's; possibly influenced by the study of continental art, he reflected the developments in European art in terms of the use of the *chiaroscuro* for the modelling of the figures' features and possibly the use of a new medium from the late 1580s [5, 6]. It is likely that Hilliard passed on to

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[9] The term miniature comes from the Latin *miniare*, meaning to decorate with red lead, which in turn derives from *luminare*, to give light. Only later the word miniature begins to indicate something small, in association with the dimensions normally used for this type of objects.

him the technique of miniatures and the art of imitating jewels. In 1605 he was appointed Anne of Denmark's limner, marking a new style in miniatures, directly linked to developments in European art. Hilliard and Oliver were very different both in approach and artistic education. While Hilliard was a great technical innovator, Oliver was consistent in established techniques and materials.

The art of miniature was a branch of art in which English artists excelled and their reputation arrived in the continent, but a serious study of early English portrait miniatures is lacking.

The Victoria and Albert Museum (V&A) in London has been interested in the materials of English miniatures attributed to Isaac Oliver (c.1565-1617) and Nicholas Hilliard (1547-1619) since many years. Further analyses were initiated in 2018, in view of the upcoming exhibition "Hilliard, Oliver and the miniature in context" at the National Portrait Gallery in London, to which the V&A was due to contribute with a select number of loans. The primary aim was the study of the materials and painting technique of the artists, to compile a technical database that could be used in future attribution studies concerning the miniatures of the late sixteenth and early seventeenth century. Additionally, the dating of production of one miniature was assessed, as it represented a wide range as timeframe. Finally, it gave the possibility to discern the presence of outliers, that is objects not related to Hilliard or Oliver, was discussed.

3.1.2 Materials and methods

Nine miniatures attributed to Isaac Oliver (Figure 3.2, Table 3.1) and three miniatures by Nicholas Hilliard (Table 3.2) of the V&A collection were investigated. Seven additional miniatures attributed to Oliver and belonging to the Fitzwilliam Museum (Cambridge) were also studied, but the results are not shown in this thesis - the V&A Science Section had indeed been commissioned a study of the FM Oliver's miniatures, to supplement other non-invasive analyses carried out by the Museum's project leads, Paola Ricciardi and Christine Kimbriel. Analysis of the Fitzwilliam Museum's miniatures was carried out as part of their ongoing research project on Oliver's materials and techniques[10] .

The technical approach of the V&A miniatures was based exclusively on non-invasive analyses, which therefore did not damage the objects or require to collect samples. All the miniatures have been documented through stereomicroscopy in order to magnify some details, including the eyes, the mouth, the decorations of the clothes and the jewels. The objects were also documented by a range of technical methods (raking light and UV fluorescence imaging, near-infrared imaging, X-

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[10] https://www.fitzmuseum.cam.ac.uk/research/secrets-silent-miniaturist-technical-analysis-isaac-oliver%E2%80%99s-miniatures

ray radiography)[11]. Subsequently, X-ray fluorescence spectroscopy and Raman microscopy were used for the identification of the pigments (Figure 3.1).

This study was carried out at the Victoria and Albert Museum, Conservation Science Section; the instruments' specifications are the following. A Leica Aristomet microscope was used to capture details of the painted areas. The microscope is equipped with three objectives (x10, x20 and x40), a x10 eyepiece and an optical zoom of up to x2.5. The XRF analysis was performed with an ArtTAX XRF spectrometer (50 kV, 600 µA, livetime 100s). The Raman analysis was performed with a Horiba Jobin Yvon XploRA microscope, equipped with 638 nm and a 532 nm diode lasers. The results described in this chapter are related only to the investigation on the flesh tones, mouths and eyes' area; however, each miniature was analysed on several details and the outcomes are reported in Appendix A.01 (complete scientific reports are stored at the V&A).

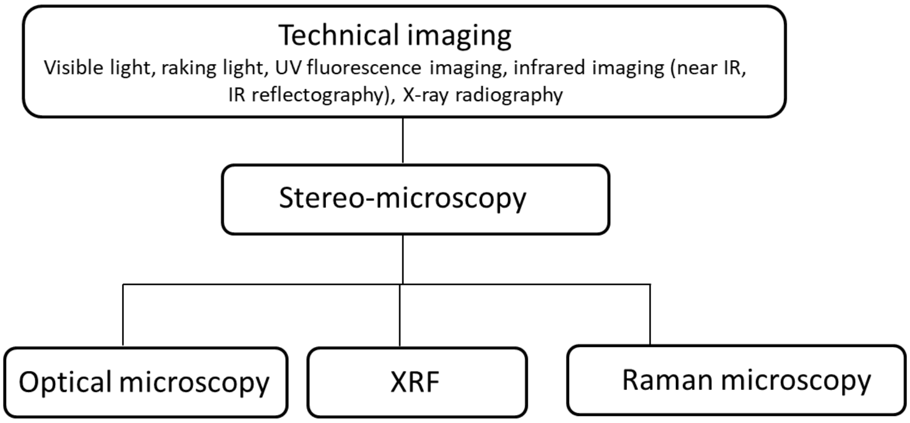

Figure 3.1. Protocol used for the technical study of miniatures.

3.1.3 Miniatures – Isaac Oliver (1560-1617)

Table 3.1. Miniatures investigated in this study; the number, description, dating and location are present, along with the analyses carried out on each one of them.

	Number	Subject	Date	V&A analysis			
				Stereo	OM	XRF	Raman
1	E.1177-1988	Robert Devereux	1596-1601	✓	✓	✓	✓
2	IS.60-1978	Unknown gentleman + Indian frame	1595	✓		✓	✓
3	P.11-1947	Unknown man	c. 1590	✓	✓		✓
4	P.41-1941	Unknown gentleman	1587-1617	✓	✓	✓	✓
5	P.43-1941	Unknown lady	1595-1600	✓	✓	✓	✓
6	P.129-1910	Portrait of an unknown gentleman	1610	✓	✓		✓
7	P.145-1910	Young girl, aged 4, holding an apple	1590	✓	✓	✓	✓
8	P.146-1910	Young girl, aged 5, holding a carnation	1590	✓	✓	✓	✓
9	630-1882	Sir Philip Sidney	1580-1650	✓	✓	✓	✓

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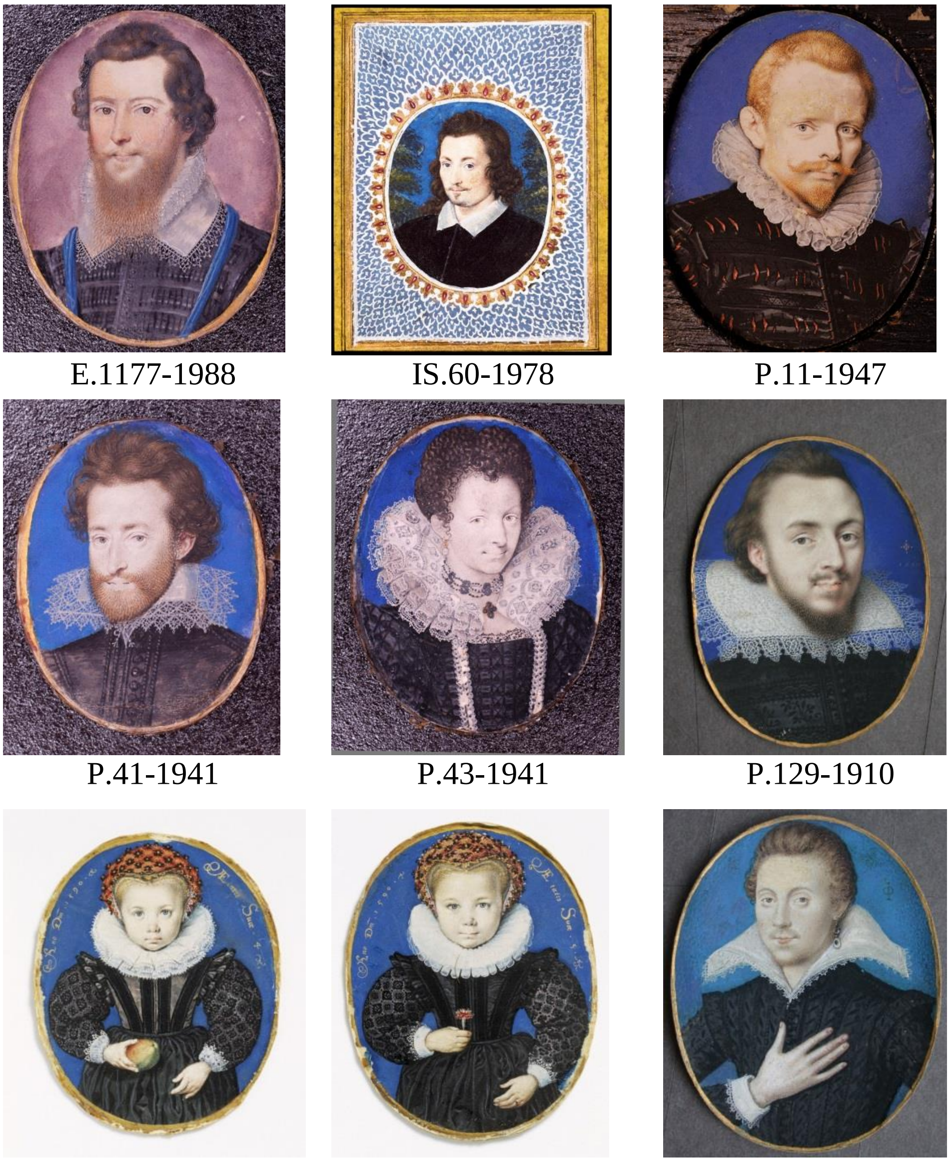
[11] Analyses carried out by the Fitzwilliam Museum and not reported in this work.



E.1177-1988 IS.60-1978 P.11-1947

P.41-1941 P.43-1941 P.129-1910

P.145-1910 P.146-1910 630-1882

Figure 3.2. Miniatures attributed to Oliver © V&A (London).

3.1.3.1. Results

Flesh tones

The flesh tones consisted of a lead white matrix scattered with carbon black particles and other pigments in order to obtain the desired hue. Red lead was identified as the predominant red component in many miniatures, with the exceptions E.1177-1988 (only one single particle was found, possibly not associated to the original mixture), where it is not present at all, and P.145-1910 and 630-1882 where it is found as the second red component after vermilion.

Vermilion was present in most miniatures (except for P.146-1910, P.41-1941, P.129-1910, P.39-1941). It was always in smaller amounts in comparison to the other components, and with small-sized particles. P.145-1910 and 630-1882 showed this pigment as the predominant one. FM 3882 contained only vermilion and no other pigments.

Other pigments were detected on the flesh tones that did not have vermilion: indigo (P.146-1910), hematite and goethite (P.41-1941), hematite, goethite and lead tin yellow type I (P.129-1910) (Figure 3.4), hematite (P.39-1941).

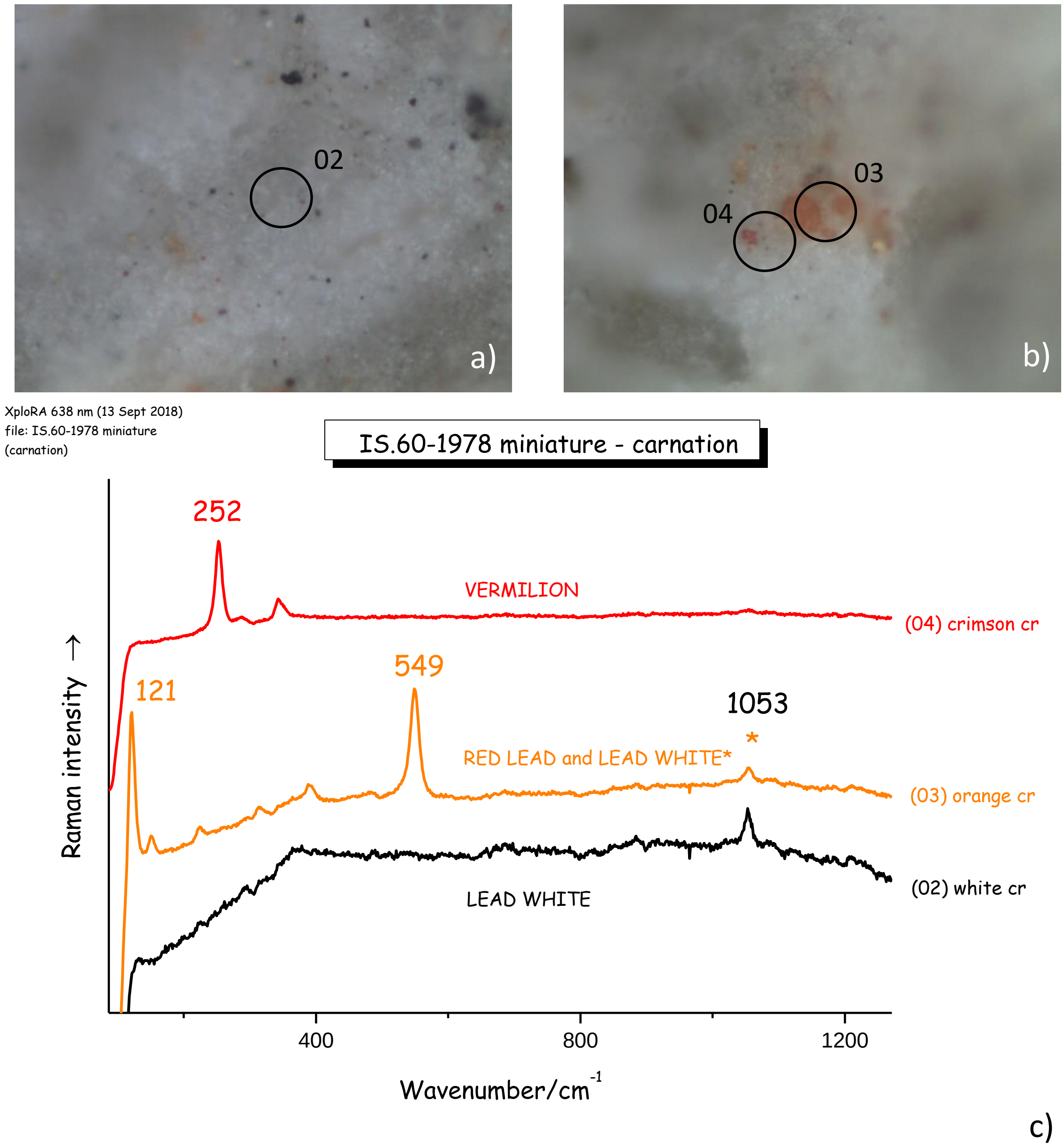


Figure 3.3. a-b) Portions of the flesh tone of IS.60-1978, viewed under the Raman microscope (500x); c) Raman spectra from the flesh tones. Lead white, vermilion and red lead are identified.

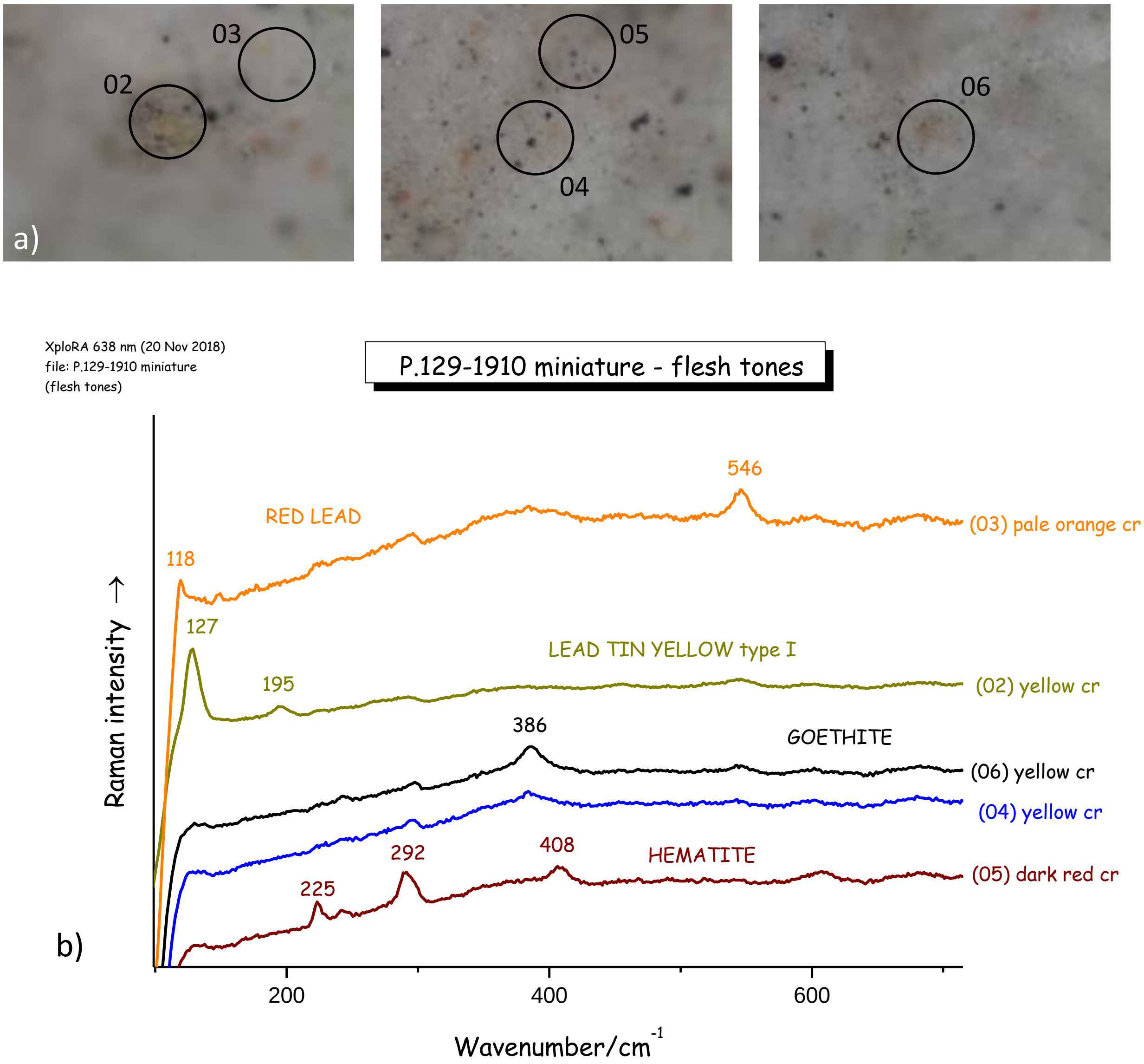


Figure 3.4. a) Portions of the forehead of miniature P.129-1910, viewed under the Raman microscope (500x). The white matrix was scattered with pale orange particles, boulder and acicular yellow ones and a few red and brown ones. b) Raman spectra from the forehead. Red lead, lead tin yellow type I, goethite and hematite were identified.

Mouths

The volume of the lips appears to be built in the same way for most of the miniatures (Figure 3.5, Figure 3.6). Two black lines, particularly visible in P.43-1941 and P.41-1941, are present at the corners of the mouth. These are covered by pink paint layers applied smoothly without any visible brushstrokes.

Red lead was used as preferred pigment, sometimes mixed with a pale pink lake; P.146-1910, P.11 and E.1177 do not present red lead.

Vermilion is present in small amount. This pigment is not present in P.129-1910 and P.39-1941, allowing to hypothesise that after 1610 was not used anymore for the lips. The exception is IS.60-1978, which did not contain vermilion but it is dated 1595. P.145-1910 and 630-1882 contained vermilion as the predominant red component. P.146-1910 consisted mostly of a pink lake and neither red lead nor vermilion were identified.

The separation line between the lips was painted at the end (because red lead and/or vermilion are underneath) with a dark pink dye.

Figure 3.5. Example of the mouth structure. Analysis sites of the mouth of miniature IS.60-1978.

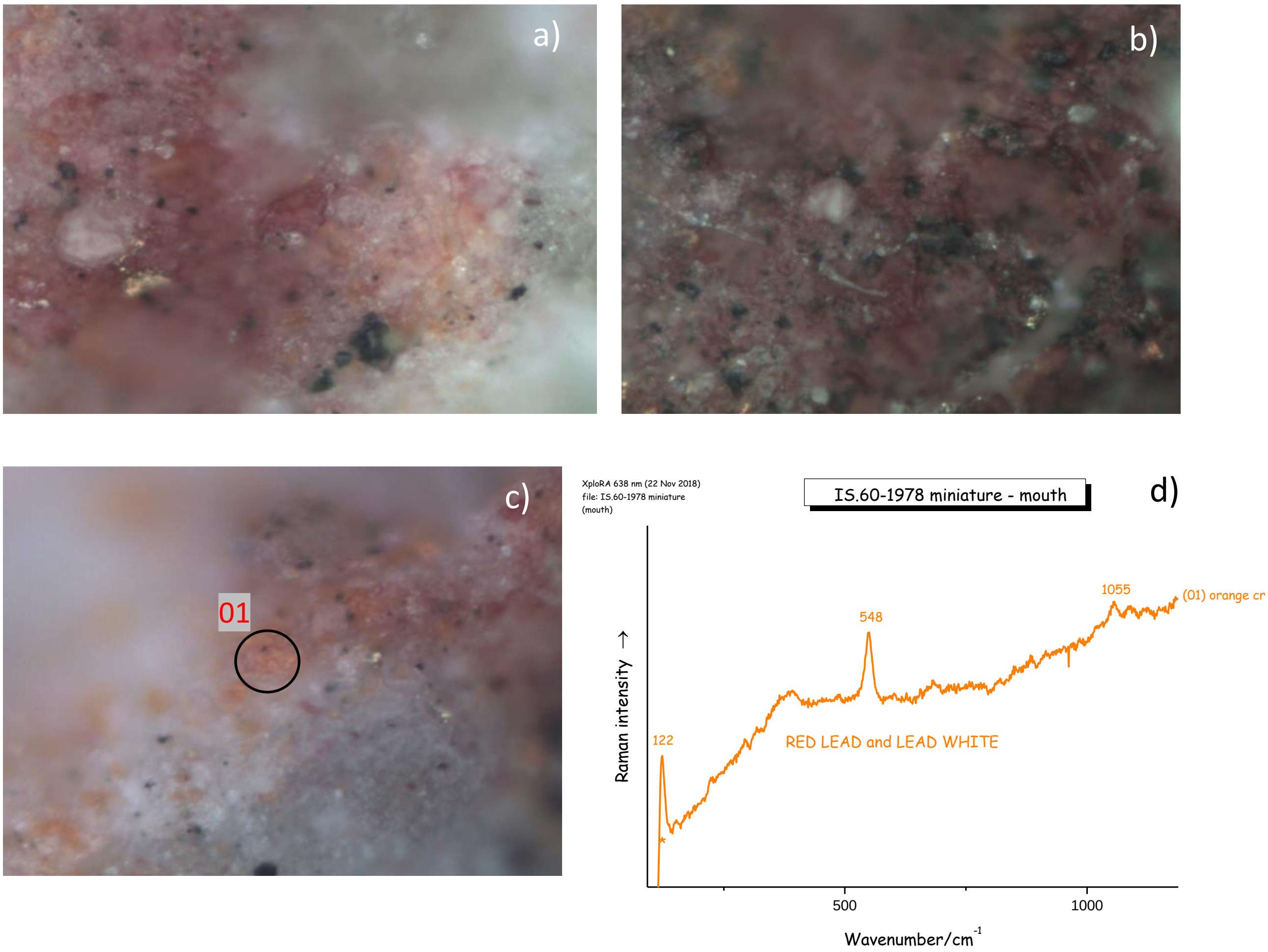


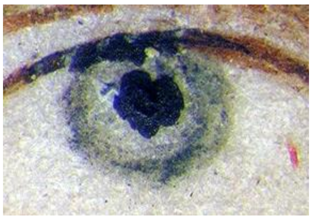
Figure 3.6. Portions of the separation line, viewed under the Raman microscope (500x): a) dark pink line (square A in Figure 3.5), b) black corner (square B); c) portion of the lips, viewed under the Raman microscope (500x), the analysed spot is indicated, and d) Raman spectrum of red lead from the lips.

Eyes' area

The results for the irises are reported in the table below and examples of the eyes' areas of four miniatures are in Figure 3.7.

Iris

The dark blue colour of the irises of miniatures P.145-1910, P.146-1910 and IS.60-1978 consisted of indigo. P.11-1941 showed indigo and carbon black and also rare vermilion particles. The grey colour of miniature P.41-1941 consisted of lapis lazuli, azurite and carbon black. The brown iris of P.43-1941, P.129-1910, E.1177-1988 and 630-1882 contained lead white, ochres (hematite and/or goethite) and carbon black. P.43-1941 contained also calcium carbonate, and P.129-1910 and P.39-1941 had red lead.

Examples of eye colour			
Colour	**Pigments identified**	**Colour**	**Pigments identified**
Dark blue 	Indigo	Grey 	No indigo, but only blue particles (azurite, lapis lazuli) and carbon black
Pale blue 	Indigo, azurite, and carbon black	Brown 	Carbon black, hematite, goethite, lead white, calcite, red lead

Inner corner

The inner corner was usually obtained with a mixture of red lead and vermilion. The presence of red lead alone was identified in P.129-1910 and P.39-1941, which dated after 1610, and in P.41-1941. The only case of mixing hematite and vermilion was in P.11-1947, where also red lead could be found.

P.43-1943 and P.146-1910 do not show any pigment in the inner corner area.

In 145-1910 a particular mixture of hematite and indigo was identified.

Eyelash lines

The eyelash lines were generally painted with two overlaid lines. The first line was made of a mixture of black and a red component, usually vermilion or hematite. In particular, hematite was found in P.129-1910, P.39-1941 and P.41-1941, when vermilion was not present. Red lead was added to hematite in P.39-1941.

The second line was darker in comparison to the first one, and made of carbon black alone. Sometimes on the proper left eye the second line is visible only in the area above the iris.

IS.60-1978 and P.43-1941 showed only one single line for the eyelashes, and it was made of carbon black. 630-1882 had one single line but it is made of carbon black and vermilion.

P.145-1910 contained also indigo other than carbon black and hematite; vermilion was not identified even if this miniature is dated 1590.

P.146-1910 does not present a red component on the outer area of the eyelash line, but only indigo and carbon black. A second red line was painted in the inner area of the eyelash line, and it consisted of red lake, carbon black and rare particles of red lead, vermilion and gold. This miniature also presented painted eyelashes (dots) on the lower eyelash lines.

Eyelid lines

The eyelid lines usually consisted of the same mixture used in the eyelash line. A first red line was applied on top of the flesh tones, with the same red component used on the eyelash line. A second black line could be seen especially at the corners of the first one, and it was made of carbon black (mixed with hematite in P.129-1910 and indigo in IS.60-1978).

Some exceptions were also present. In two cases the eyelid line presented an additional red pigment in comparison to the mixture used in the eyelash line. IS.60 showed a red eyelid line, made of vermilion and red lead, while the eyelash was a single black line.

P.129 had a slightly different build-up in comparison to the eyelash line. The eyelid consisted of two lines: the first one was yellow and made of goethite, the second one applied on top was red and made of hematite. P.11 showed an eyelash line made of vermilion only, while the eyelid line was slightly different and consisted of a mixture of hematite and vermilion; moreover, these two pigments were usually not mixed together. P.145-1910 contained hematite, indigo and carbon black, and not vermilion. P.146-1910 did not present a red component and it also consisted of a single line. Finally, between the eyelash lines and the eyelid lines red lead particles could be seen for most of the miniatures.

P.41-1941 FM 3869

Figure 3.7. Examples of the eyes' area of two miniatures.

3.1.3.2. Discussion: Isaac Oliver's materials and technique

The overall trend for Isaac Oliver's materials and technique is consistent for most of the miniatures analysed and dated from 1588 to 1615. Traditional pigments, such as lead white, red lead, hematite, vermilion, azurite, lapis lazuli, indigo, goethite and carbon black, are commonly used for several areas of the objects. A few pigments are only occasionally used, such as pararealgar and lead tin yellow type I, smalt and massicot in P.145-1910 (see Appendix A).

Moreover, the timeline based on the dating proposed by stylistic research (Figure 3.8) was compared with a new one that takes into account scientific results (Figure 3.9). In this way, the date of production of one miniature was assessed; moreover, the results collected on a few miniatures raise doubts about the attribution to Oliver and further study may be required in order to understand if these objects are made by other artists or are Oliver's outliers.

Flesh tones

Oliver's technique for the flesh tones consists of a mix of lead white, carbon black and other pigments. Usually red lead is the main red component, occasionally mixed with rare, small-sized vermilion particles. After c. 1610 vermilion seems to be replaced by other pigments, like hematite, goethite and lead tin yellow type I, providing the grounds for a chronological difference.

Mouth

The structure of the mouth is constant for the whole period under study. The lips are obtained with red lead, sometimes mixed with a pale pink lake or vermilion; two black modelling lines are always present at the corners of the mouth; a separation line between upper and lower lip is applied at the end of the painting process using a dark pink lake. Also in this case vermilion is not present after c. 1610.

Eyes

The eyes' contour was investigated in several areas. The inner corner of the eyes is usually obtained with a mixture of red lead and vermilion; after 1610 red lead is the only pigment identified. The eyelash lines and the eyelid lines are generally made of two overlaid lines. In particular, the eyelash lines consist of a first line made of a black and a red component (vermilion is present only until 1610), while the second one is made of black particles only. The eyelashes are painted only at the outer edge of the upper eyelash line, and on the proper right eye (they are especially visible in the female portraits). The eyelid lines are made of a first red line, consisting of the same red pigment of the eyelash line, and only at the corners of this line a second black line is visible. Moreover, some red lead applied between the eyelash and the eyelid lines is always visible.

Assessment of the date of production

P.41-1941

The dating range of P.41-1941 was 1587-1617. The absence of vermilion in all the areas analysed (flesh tones, mouth, inner corner, eyelash lines, eyelid lines) on this miniature would allow to restrict the period to 1610-1617.

Doubts about the attribution

E.1177-1988

This miniature has been heavily retouched in the 19th century, but we managed to analyse areas which are considered original, following an examination under UV. Unusually, this object does not contain red lead on the flesh tones or the mouth, while this is usually the predominant coloured pigment in those areas. We cannot confirm or disprove that some red lead may be present in the mouth and it simply cannot be seen because it is covered by an organic red lake. The attribution to Oliver can be considered uncertain, or it can be said that this miniature is an outlier.

P.11-1929

This miniature is dated 1590 and shows a mixture of the flesh tones characteristic of Oliver’s technique of this period. However, the mouth contained only vermilion, while red lead, which is always the predominant element in this area in other miniatures, was not identified nor was it visible. Moreover, the inner corner of the eyes and the eyelid lines were obtained with a mixture of hematite and vermilion, which was never observed on the other Oliver miniatures. However, E.1178-1988, painted by Hilliard and dated 1580-85, contained this mixture in the flesh tones. FM 3868 presented vermilion and hematite but not mixed together (vermilion was part of the flesh tones’ composition and hematite was applied only on the redder areas to achieve the desired hue). For these reasons the attribution to Oliver may perhaps be reconsidered.

630-1882

Vermilion was the predominant component in the flesh tones and mouth, instead of red lead as normally found. The inner corner consisted of an unusual mixture of several pigments (vermilion, red lead, azurite and carbon black). The eyelash line was made of a single line and contained a mixture of carbon black and vermilion, which is never found in the other miniatures (normally when the line is single it is made of carbon black only). The attribution to Oliver can be excluded.

Outliers

IS.60-1978

This miniature is dated 1595 but does not contain vermilion in the mouth's mixture, which could be considered an exception. The presence of indigo mixed with other pigments in the inner corner of the eyes and in the eyelid lines is also unusual. An Indian frame was added around this object at a later time. The miniature was possibly retouched as well (for example, are the trees in the background original or a later addition?), making it difficult to assess the originality and authenticity of the pigment mixtures.

P.145-1910

Vermilion was the predominant component in the flesh tones and the mouth, mixed with only a few red lead particles. The eyelash lines and the eyelid lines were made in a similar way; a first line of carbon black, hematite and indigo and a second one of carbon black only.

P.146-1910

The flesh tones contained mostly red lead, mixed with indigo and rare pararealgar; the absence of vermilion may indicate a creation after 1610, following the general trend, or an exception. Moreover, no red lead or vermilion was identified on the mouth, which consisted mostly of a pink lake/dye mixed with azurite, carbon black and gold. The eyelash line consisted of two parts: the outer one was made of carbon black and indigo, the inner one was red. Some dots on the lower lid indicating the presence of eyelashes were also visible.

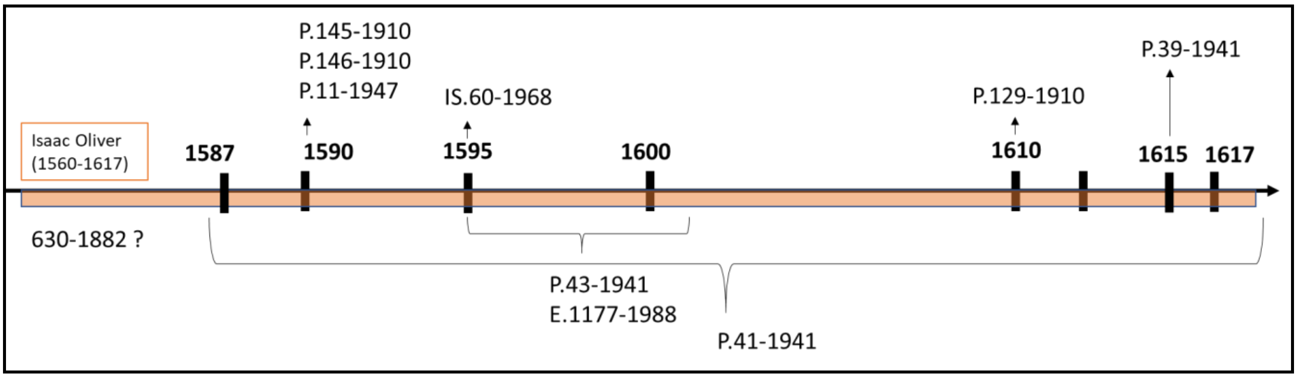


Figure 3.8. Timetable of the miniatures painted by Oliver with the chronological attribution based on stylistic information. P.41-1941 shows a large timeframe, 630-1882 is not dated.

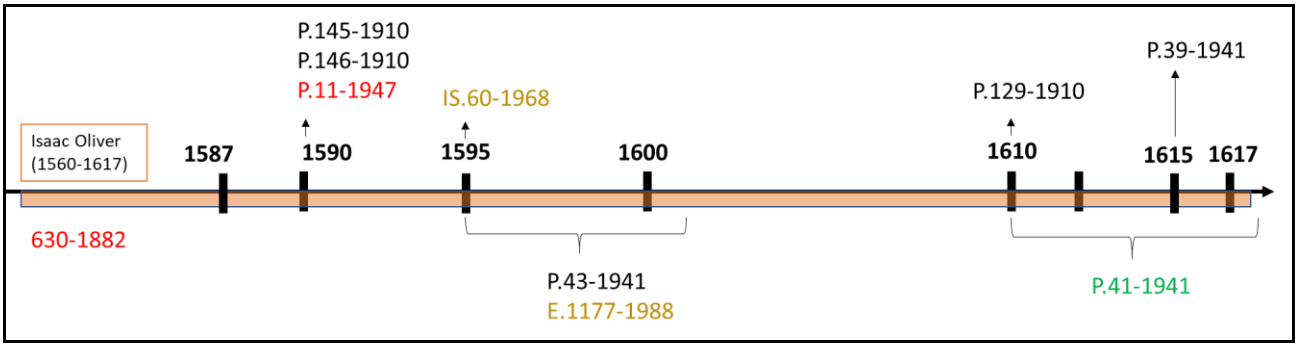


Figure 3.9. Proposal of a new timetable. The proposed new dates are indicated in green: P.41-1941's date is narrowed down to 1610-1617. The miniatures of dubious attribution are shown in red. The miniature with suggested 'wobbly' attribution is in yellow.

3.1.4 Miniatures – Nicholas Hilliard (1547-1619)

Table 3.2. Miniatures investigated in this study; the number, description, dating and location are present, along with the analyses carried out on each one of them.

	N.	Subject	Date	Collection	V&A analysis			
					Stereo	**OM**	**XRF**	**Raman**
1	E.1178-1988	Unknown man	1580-85	V&A Museum	✓	✓	✓	✓
2	P.5-1944	Unknown man	1597	V&A Museum	✓		✓	✓
3	P.8-1945	Unknown lady	1590	V&A Museum	✓	✓	✓	✓

E.1178-1988

P.5-1944

P.8-1945

3.1.4.1. Results

Flesh tones

The flesh tones consisted of a lead white and carbon black matrix scattered with red pigments. Red lead was found on all miniatures.

P.8-1945 contained also a few particles of azurite. Blue pigments were not identified in the miniatures of the male sitters, which had additional red pigments (hematite in P.5-1944 and vermilion and hematite in E.1178-1988).

Lead tin yellow type I was also identified in P.5-1944 and goethite in P.8-1945.

Finally, the flesh tones of E.1178-1988 appeared very different when viewed under a microscope in comparison to the other miniatures: it contained many red and black particles, while the others had a simpler palette and only a few scattered red particles (Figure 3.10, Figure 3.11).

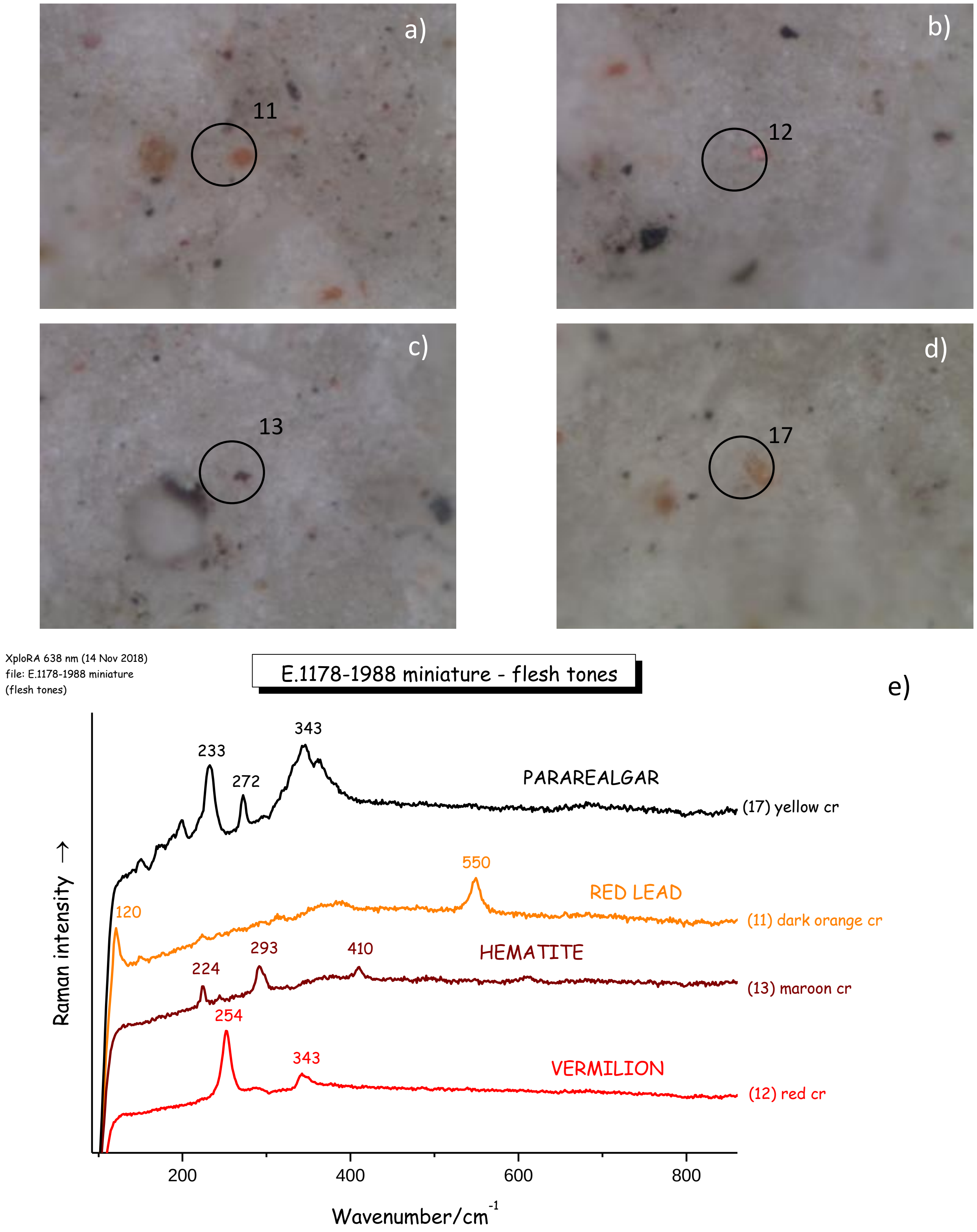


Figure 3.10. a-d) Portions of the forehead of E.1178-1988, viewed under the Raman microscope (500x). e) Raman spectra from the forehead: vermilion, hematite, red lead and pararealgar were identified.

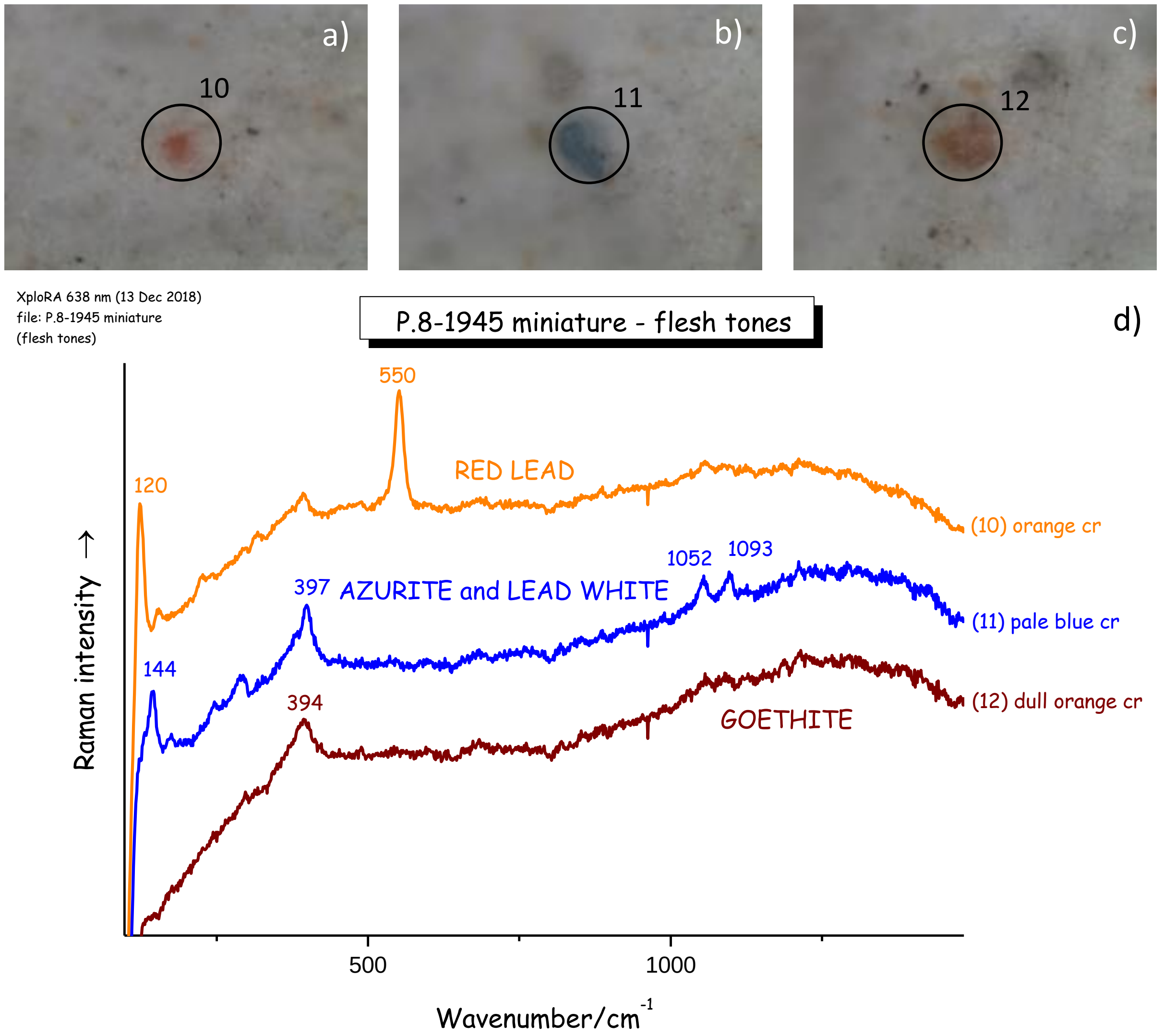


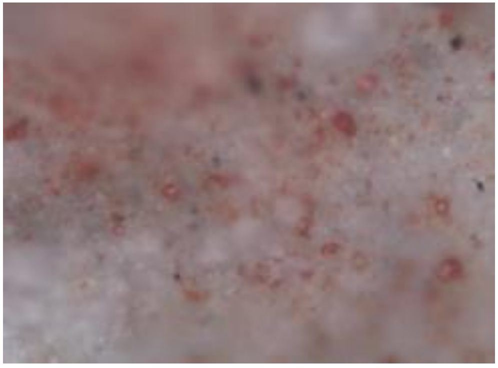
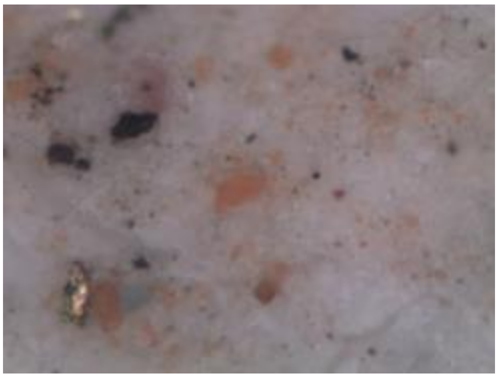
Figure 3.11. a-c) Portions of the flesh tones of P.8-1945, viewed under the Raman microscope (500x); d) Raman spectra from the forehead. Red lead, azurite, lead white and goethite were identified.

Mouth

In P.8-1945 two brown spots were visible at the corners (see table below), the lips contained red lead covered by a pale pink lake and a separation line was made of a darker pink lake.

The mouth of P.5-1944 consisted of vermilion; carbon black and a pink dye were also present.

The mouth of E.1178-1988 was covered by the moustache and was not entirely visible, but it contained red particles with the appearance of vermilion, mixed with a pale pink dye and black particles of probably carbon black.

Nr.	Area investigated (40x)	Photo of the lips under Raman microscope (500x)
P.5-1944		
P.8-1945		

Eyes

Iris

The grey/pale blue irises of E.1178-1988 and P.5-1944 were made of indigo and carbon black (and brown pigments in P.5-1944). The brown iris of P.8-1945 consisted of carbon black and possibly a brown pigment.

Inner corner

The inner corner was made of a red component (pink lake, vermilion, red lead), which is different for each miniature.

Eyelash line

The eyelash lines were usually two overlaid lines: the lower one was lighter and the upper one darker (see table below). P.5-1944 and P.8-1945 were built in the same way, with a first line made of carbon black and brown pigments and a second one which contained carbon black. In E.1178-1988 a first red line (made of vermilion) was covered by a second darker one (black, made of carbon black in an organic layer. In E.1178-1988 the brushstroke seemed continuous, while in the other objects the line is made of several dots. In P.8-1945 the lower eyelash line was painted with dots to show the presence of eyelashes.

Eyelid line

The eyelid was made of a single line of the same pigments used for the eyelash line.

The eyelid line consisted of carbon black for the miniatures P.5-1944 and P.8-1945, with more finely divided particles in comparison to the eyelash lines. E.1178-1988 had a red line of the same pigment used for the eyelash.

No red lead was found in the area between the eyelash and the eyelid lines.

Eyebrows

The eyebrows were obtained with carbon black mixed with a brown pigment (not identified) and/or iron oxides.

	PR eye (40x)	PL eye (40x)
E.1178-1988		
P.8-1945		

3.1.4.2. Discussion: Nicholas Hilliard's materials and technique

Only three miniatures painted by Hilliard in a narrow chronological range (from 1580-85 to 1590) were studied and therefore the results are not comprehensive.

Several traditional pigments are identified (see Appendix A.01): lead white, calcite, carbon black, vermilion, hematite, red lead, pararealgar, lead tin yellow type I, goethite, indigo and azurite. The presence of organic dyes is also suggested, in particular pale pink, dark pink and yellow dyes. Massicot is identified only in P.8-1945.

Flesh tones

The lead white matrix of the flesh tones is scattered with a few carbon black and red lead particles. Vermilion is identified only in E.1178-1988. A possible difference is encountered in the flesh tones of the male sitters, where hematite is found, in comparison to the female ones, where azurite is identified. Yellow pigments are present in both male and female portraits (lead tin yellow type I in P.5-1944 and goethite in P.8-1945).

Mouth

The structure of the mouth is consistent for all miniatures (except E.1178-1988 where the lips are covered by the moustache). At the corners two black/brown spots are visible.

Eyes

The inner corner is painted with a single red pigment (pink lake, red lead or vermilion), different for each miniature studied. Therefore in this case a trend is not assessed.

The eyelash lines consist of two overlaid lines: the first line is lighter and the second, upper one is darker or black. Dots seems to be present in the lower eyelash line (under the iris) in the woman's portrait (P.8-1945) to suggest the presence of eyelashes. The eyelid lines are normally painted in a single line and with the same pigments used for the eyelash lines, but with a more finely divided size. No red lead was identified in the eyelid area.

3.1.5 Conclusion: comparison between Oliver and Hilliard

A comparison between Oliver's materials and technique with Hilliard's was attempted, based on the only three Hilliard miniatures studied in this occasion.

Oliver's flesh tones are characterised by the presence of red lead as the predominant pigment, mixed with only vermilion before at least 1610 and with hematite and other pigments after 1610. Hilliard uses vermilion only in E.1178-1988 (in a mixture of red lead, vermilion and hematite, which Oliver never made) and not for the other three miniatures. Moreover, while Oliver do not differentiate between male and female sitters in terms of materials, a possible difference can be found in Hilliard's male portraits, where hematite is present, and female ones, where azurite is identified.

Moreover, even if the structure of the mouth seems similar in both Oliver and Hilliard, there are small elements that can be used to differentiate the works of the two artists. In Hilliard, the corners appear of brown colour and less marked in comparison to the black ones painted by Oliver. It seems there is also a difference in the pigments Hilliard used for the lips for the male portraits (where vermilion is identified) and the female ones (where red lead mixed with a pink dye is found). Oliver used red lead for all the sitters' lips.

In terms of eyes contour, the inner corner is always painted with a mixture of red lead and vermilion in Oliver's miniatures before 1610 (only red lead after 1610) but with different single red pigments in Hilliard (red lead or vermilion or a pink dye).

The brushstrokes are made of several dots in Hilliard's eyelash and eyelid lines, while Oliver seems to apply continuous lines. Moreover, in Hilliard's female portrait P.8-1945 the eyelashes are painted in the lower eyelash line with several dots, while in Oliver the eyelashes are present in the upper eyelash line and only at the outer edge of the eyes.

Another difference is the absence of red lead in the area between the eyelash and the eyelid in Hilliard's objects, which is always present in Oliver's and probably applied in order to create volume.

Finally, there is only a single line for the eyelid line in Hilliard's works, made of the same pigments used for the eyelash line but more finely divided, while in Oliver it can be two overlaid lines.

In conclusion, it can be argued that Hilliard and Oliver can be potentially differentiated from a material and technique point of view, but further studies on Hilliard's miniatures are required in order to assess his trends more systematically and propose a more comprehensive comparison between the two artists.

3.2 Micro-invasive analyses – Gianpietrino paintings

3.2.1 Introduction

Giovan Pietro Rizzoli, the Milanese painter known as Gianpietrino, is considered one of the most prolific interpreters of Leonardo's legacy in Lombardy [7]; at the same time, concerning biographical aspects, he is one of the less known subjects. He was probably born between 1480 and 1485, entering the da Vinci’s workshop in the second half of the 1490s; it is believed that his death took place in 1553.

The fame and notoriety linked to the figure of this painter has meant that the name of Gianpietrino became a sort of 'container' over time: the *corpus* of artworks has reached a too wide an extent and part of it is certainly referable to collaborators and followers. One of the greatest difficulties in the reconstruction of his style and technical evolution is due to the lack of secure chronological aspects; the *Madonna with Child between Saint Jerome and Saint John*, known as Pala Fornari and painted in Pavia (Italy), is the only artwork confidently attributed to Gianpietrino that shows the year of execution, as the date 1521 is written on the frame.

Gianpietrino, influenced decisively by Leonardo – who was present in Milan during the last two decades of the 1400 and again from 1506 to 1513 -, makes his own many of the Master’s teachings, nurturing his art with compositions, iconography, technique and Leonardoesque pictorial effects.

One of the examples that underlines the close relationship between pupil and Master is the painting *Saint Mary Magdalene with a sarcophagus* in a private collection [8], as it is inspired by the studies of Leonardo da Vinci for the same saint. In fact, in a sheet kept at the Courtauld Institute of Art in London (Seilern collection), two Leonardo drawings dated around 1480-1482 depict two different types of Mary Magdalene. The second one in particular seems more dynamic, with the hair loose on the shoulders and looking directly at the observer; it is this second version that Gianpietrino tries to translate into a painting.

Moreover, this painting of Saint Mary Magdalene has seen an alternation of proposed dating, sometimes contradictory. For this reason, the research aims to highlight, through a comprehensive methodology with a multi-analytical approach, how the painting can be counted among the early works of Gianpietrino.

Three other paintings attributed to this artist were then investigated, to gather information about the evolution of materials and pictorial technique, useful for future attribution questions. The three artworks specifically are the *Madonna with Child* of the Rijksmuseum of Amsterdam, the *Martyrdom of Saint Catherine* (Museo Ideale, Vinci) and the *Madonna with Child between Saint*

Jerome and Saint John of the Archbishopric of Pavia (Italy), which is the only work dated by the artist.

After a first evaluation of the paintings' condition, using raking light and UV photography, IR reflectography was performed for the investigation of the preparatory drawing, while XRF gathered information on the pigments present. For two paintings, namely, Sai*nt Mary Magdalene* and *Madonna with Child*, X-ray radiography was also performed.

Following this procedure, sampling locations were identified and cross-sections prepared. The protocol applied to these samples consisted in a first documentation by optical microscopy both in visible and UV, and subsequently the use of SEM-EDS, FTIR and Raman microscopy for the characterisation of inorganic and organic components of each layer. In this way, information on the materials constituting the artworks is gathered, together with new insights about the technical execution and degradation products.

Finally, following the evolution of Gianpietrino's painting technique, it was possible to carry out a comparison with Leonardo's particularly in terms of the flesh tones, comparing the data with the edited ones (De Viguerie, Walter, Laval, Mottin, & Sole, 2010; Mottin, Menu, & Mohen, 2006).

3.2.2 Materials and Methods

Paintings studied

Four paintings attributed to Gianpietrino were considered in this study and are indicated in Table 3.3 along with their characteristics (technique, type of support, dimensions), collection and date of attribution based on stylistic studies and on the provenance. The scientific analysis performed on the objects are summarised in Table 3.4 (Figure 3.12). Visible photography, infrared reflectography, X-ray radiography and the preparation of cross-sections for *Madonna with Child* (P2) were carried out by the Rijksmuseum of Amsterdam.

Table 3.3. Paintings studied with their characteristics, date of attribution and collection.

Painting	**Description**		**Painting**	**Description**
 **P1**- Saint Mary Magdalene with a sarcophagus	tempera and oil on poplar panel, 63.5x 8.3 cm 1515-20 1510-20 1520-30 Private collection, Russia		 **P2 -** Madonna with Child	oil on poplar(?) panel, 65.6x53x0.8cm 1510-15 Rijksmuseum of Amsterdam
 **P3 -** Martyrdom of Saint Catherine	oil on panel 1500-15 Private collection, (preserved at the Museo Ideale, Vinci)		 **P4** - Madonna with Child between Saint Jerome and Saint John	oil on poplar panel, 213x160cm 1521 Archbishopric of Pavia (Italy)

Table 3.4. Analyses carried out on the paintings.

	Non invasive					**Micro-invasive (cross-sections)**		
Painting	**VIS**	**UV**	**IRR**	**X-ray R**	**XRF**	**SEM-EDS**	**FTIR**	**Raman**
P1	✓	✓	✓	✓	✓	✓	✓	
P2	✓		✓	✓		✓		
P3	✓	✓	✓		✓	✓		✓
P4	✓	✓	✓		✓	✓	✓	✓

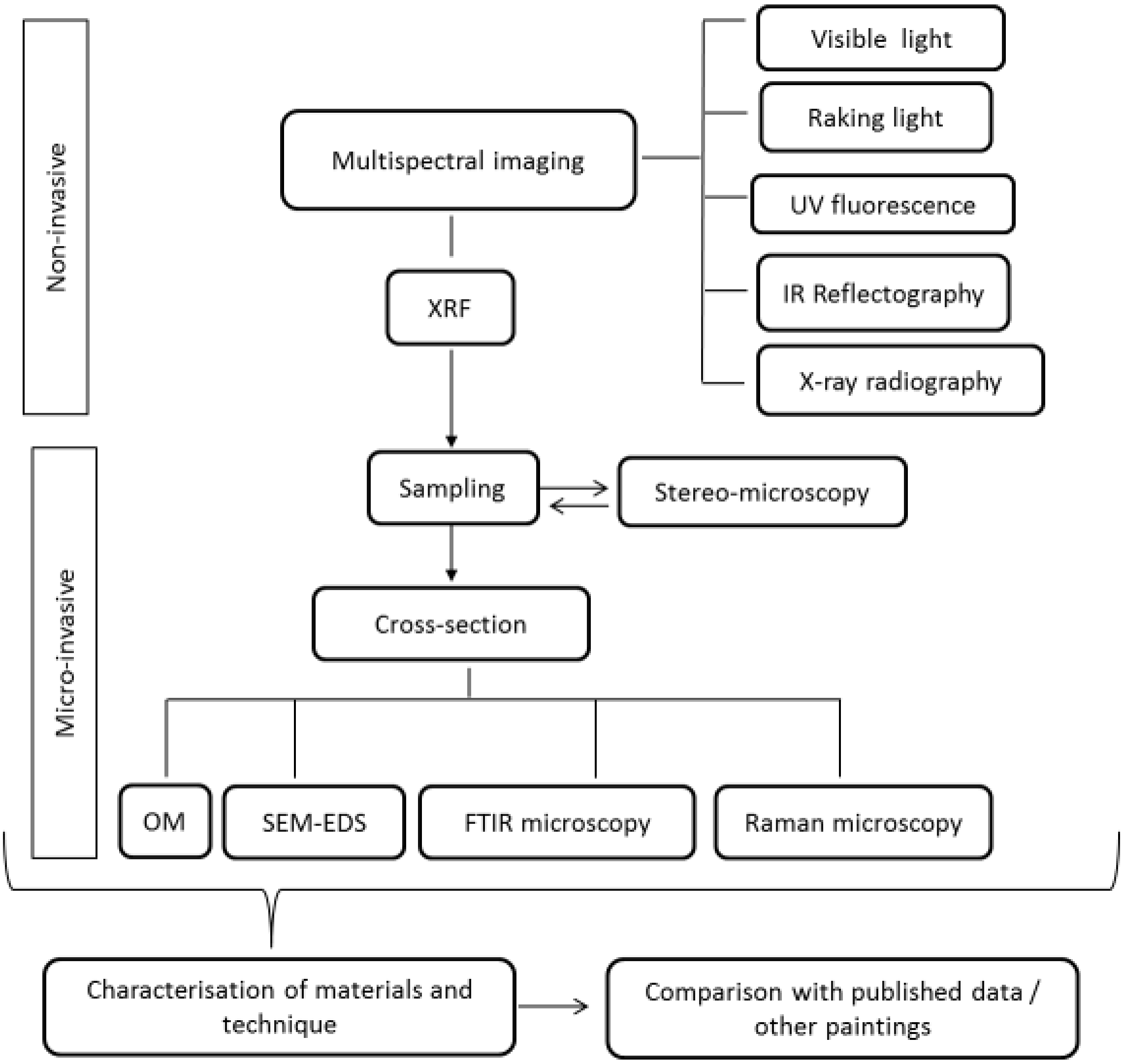


Figure 3.12. Proposal of a protocol for the study of paintings.

3.2.3 Results and discussion

By means of raking light and UV fluorescence, the state of conservation of the four paintings is assessed. All of them were in a good state, several restorations during the time are also present.

All the pigments suggested by XRF were traditional in the 16th century and therefore compatible with the lifespan of Gianpietrino.

The preparatory drawing (images reported in Matteucci, 2016) is normally characterised by charcoal lines, sometimes retraced with a fluid medium in some areas, mostly in the faces and in the *chiaroscuro*. Traces of pouncing were visible in the Child's face of P2. Various *pentimenti* have been found, especially in the outline of the hands, while a significant change of position of the

Virgin's head in P2 was detected, in addition to a lowering of the neckline of her dress. Moreover, various interventions made by the artist were noted on the size and shape of the jar held by Mary Magdalene (P1).

X-ray radiographies show how the hands of Mary Magdalene (P1) and the Virgin with Child (P2) appear rather stiff and the fingers are marked by continuous white brushstrokes. In addition, earlier compositions in both paintings are clearly recognisable. The X-ray radiography of Mary Magdalene (P1) is particularly interesting as the lower part of the dress and the left hand of the saint appear completely painted, but this first composition was covered at a later time by the sarcophagus. The Virgin's head (P2) was previously painted in a more static and classic position, then changed with a slightly bending of the face towards the Child; it is remarkable that various copies of the Leonardo's *Madonna of the Yarnwinder* [11] exhibit the same position of the head: the Virgin, supporting the Child, directs her gaze to him with half-closed eyes.

The characterisation of the inorganic and organic component through the use of different analytical techniques on cross-sections will be treated separately for each painting. The aim is to gather information on the original materials constituting the artworks and the degradation products, the executive technique and the evolution over time, allowing, finally, a comparison with Leonardo's technique.

Ground layer

The ground of each painting analysed by SEM-EDS consists of calcium and sulfur; the intense FTIR band around 1100 cm^{-1} and the others at 1618, 1680, 3390, 3519 cm^{-1} identify gypsum (calcium sulfate di-hydrate) (Figure 3.13). The bands at 1650 cm^{-1} (amide I) and 1538 cm^{-1} (amide II), when visible, are characteristic of a proteinaceous compound, such as animal glue. A thin layer of proteinaceous material is laid on top of the ground, which helped to prevent the absorption of the binder of the pictorial layers through the porous gypsum of the ground. In P1, a few particles of strontium and sulfur in the white ground suggest the presence of celestine (strontium sulfate, $SrSO_4$), a gypsum impurity [12].

The ground of P2 was not sampled, but some traces are visible in the orange sample and constist of Ca and S, possibly related to gypsum.

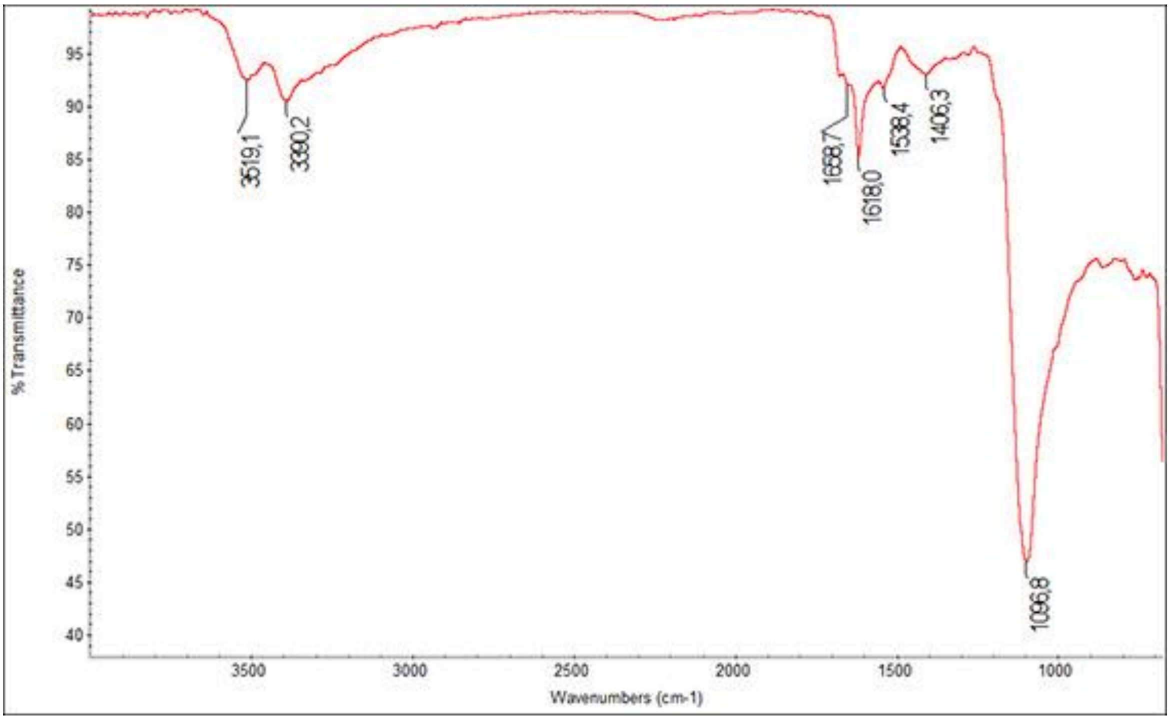


Figure 3.13. FTIR spectrum collected on the ground of P1.

Imprimitura

The priming layer (or *imprimitura*) applied on top of the ground varies for the materials, the colour and the location (Figure 3.14). Mary Magdalene (P1) and the Madonna with Child (P2) present a white *imprimitura* under the green and blue areas, but not under the flesh tones and the background, perhaps with the aim of using the white layer to make the blue and green areas brighter. The layer consists of lead, likely linked to lead white, and confirmed by the FTIR absorptions (on P1) at 3530, 1390, 1043, 848, 766 cm^{-1} (in particular, as a mixture of cerussite and hydrocerussite). The bands at 2920, 2850 and 1730 cm^{-1} are associated to a drying oil, and the one at 1520 cm^{-1} is related to lead carboxylates and therefore to the degradation of the lipid binder [13].

Saint Catherine (P3) and the altarpiece of Pavia (P4) show a grey *imprimitura* present under all the analysed samples and hypothetically overall the surface of the artworks (as documented in *Christ carrying the cross* (1510-1530) and *Salome* (around 1510-1530) of the National Gallery in London [14]). The use of this priming presumably plays a key role in obtaining the desired finale hue. The layer contains mostly Pb, while a few black particles scattered around the matrix were made of carbon, and possibly linked to carbon black. FTIR absorptions on both samples at approximately 3535, 1385, 838 cm^{-1} identify lead white (hydrocerussite and cerussite) and the peaks at 2920, 2850 and 1730 cm^{-1} are related to a drying oil. In P3 calcium carbonate and silicates are identified as well.

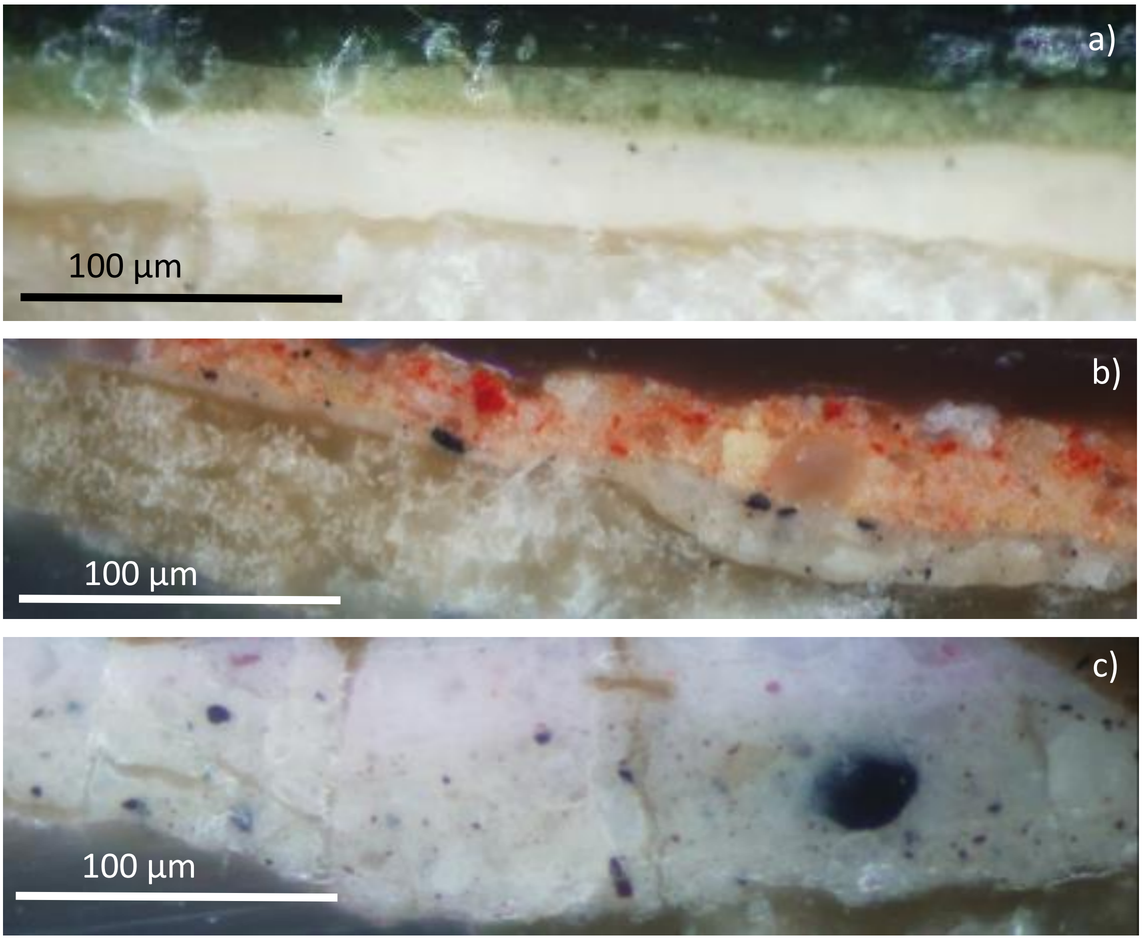


Figure 3.14. a) White priming of St Mary Magdalene (P1); b) grey priming of St Catherine (P3) and c) Pavia's altarpiece (P4).

Green pigments

The green layers of P1 and P2 consist of a first light green layer followed by a darker one. P2 was analysed only by SEM-EDS, therefore a thorough characterisation was not achieved. The lower, lighter layer of P1 and P2 contains copper and lead; FTIR analysis on P1 shows the absorption approximately at 1550 cm^{-1}, related to verdigris, possibly as basic copper acetate [15], while the bands at 1398 and 838 cm^{-1} confirms the presence of lead white. The binder is identified as a drying oil (absorptions around 2920, 2850, 1734 cm^{-1}), with the presence of free fatty acids (1715 cm^{-1}) and copper carboxylates (1585 cm^{-1}) [13, 16]. The second green layer consists of verdigris (1550, 1413 cm^{-1}) and a small amount of lead white (838 cm^{-1}), while the peaks at 1585 and 1460 cm^{-1} are associated to copper carboxylates and the one at 1660 cm^{-1} is related to copper oxalates [15] (Figure 3.15). The upper, darker layer of P2 contains only copper and not lead.

In the Pavia's altarpiece (P4) three pictorial layers are found. The first two are of light green colour and the third is dark green. In particular, the first light green layer is a mixture of verdigris (absorption at 1555 cm^{-1}) and lead white (1392, 835 cm^{-1}), the second and the third do not show lead white but only verdigris (Figure 3.16).

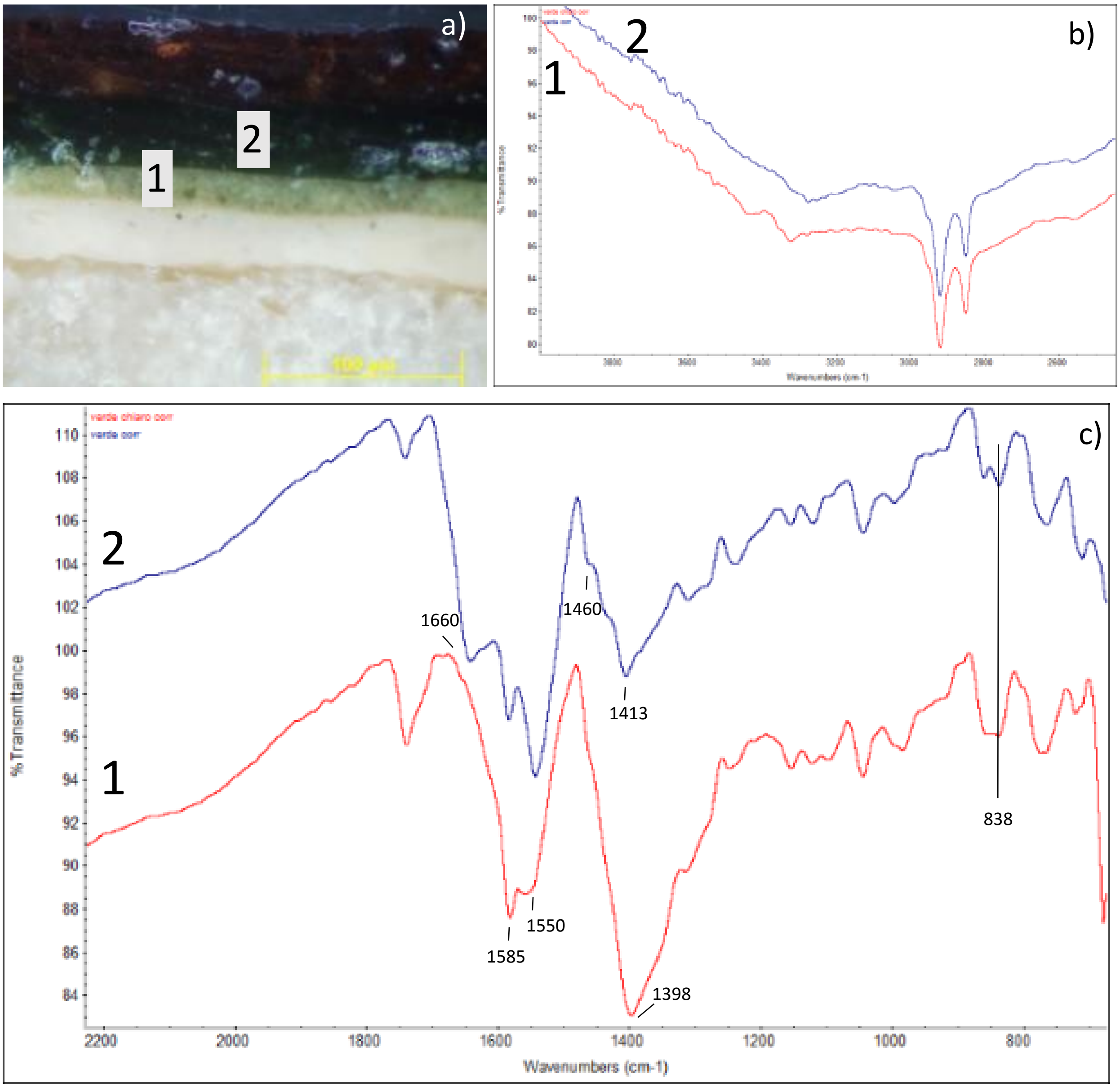


Figure 3.15. a) Cross-section of the P1 sample collected on the sarcophagous: two green layers, associated to the green dress, are visible and on top of them the red layers of the sarcophagous; b) FTIR spectra of the layers 1 and 2 in the range 4000-2400 cm^{-1} and c) 2200-750 cm^{-1}.

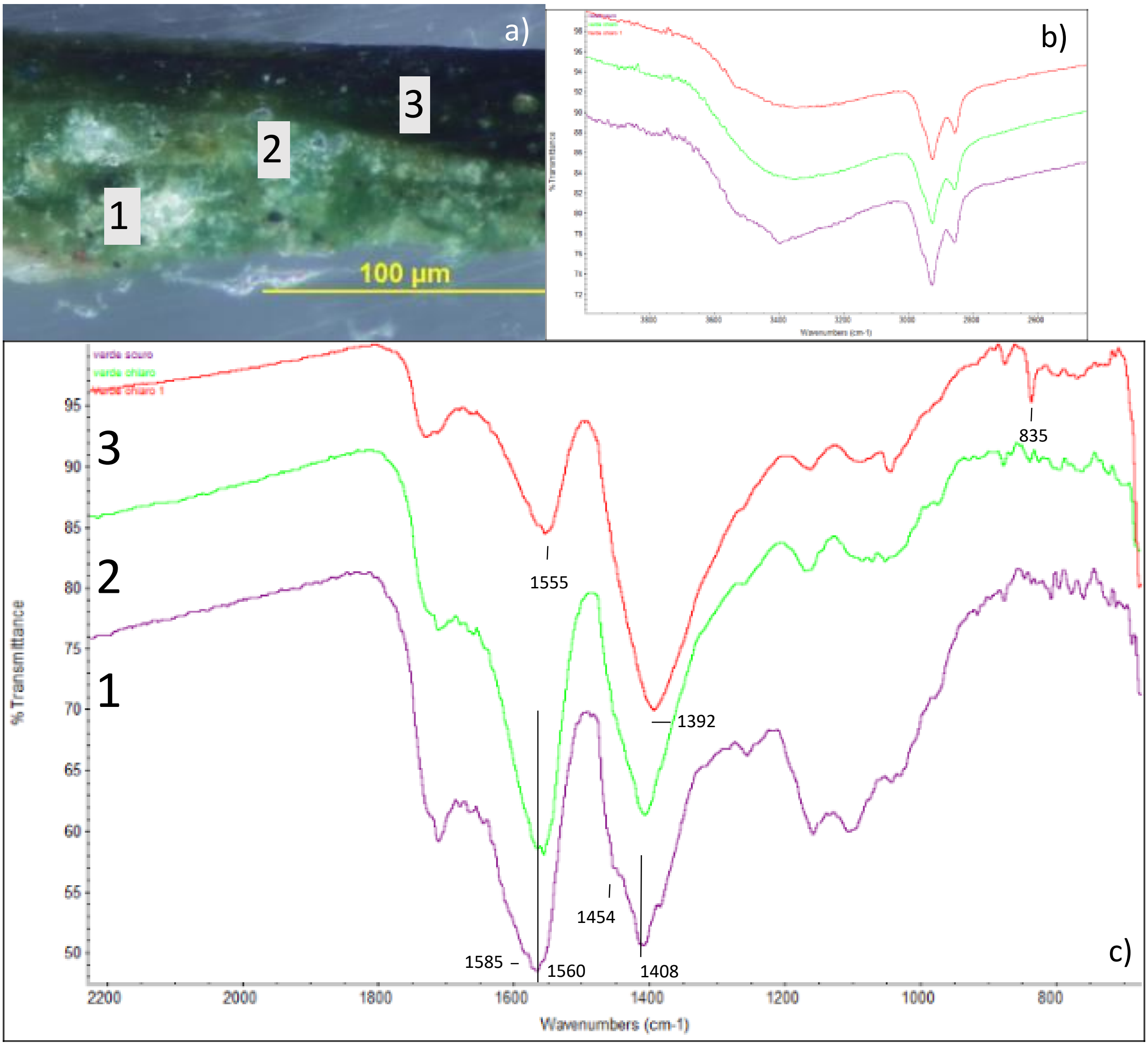


Figure 3.16. a) Cross-section of the P4 sample collected on the green: two light green and one dark green layers are visible; b) FTIR spectra in the range 4000-2400 cm^{-1} and c) 2200-750 cm^{-1}.

Orange pigments

The orange colour usually consists of a mixture of red and yellow pigments; lead white and carbon black are added to modulate the hue.

P1 does not have an orange area and therefore no sample was collected, but the yellow area of the jar consisted mostly of Fe, likely linked to ochres. P2’s orange cross-section shows several grains of different colour within the single layer. The orange ones are Fe-based and possibly identified as red/orange ochres, the red ones are made of Hg and S, likely to be vermilion, the black ones contain Ca and P, probably associated to bone black; C and Al on a few red grains suggest the presence of a red lake, where the colourant precipitated on an alumina substrate. Lead is also identified, and it is possibly associated to lead white, even if the use of lead oxide cannot be excluded.

The orange sky of the Saint Catherine (P3) presents a single orange layer. It consists of a mixture of vermilion (Raman bands at 254, 344 cm^{-1}) and lead tin yellow type I (130, 197, 289, 450 cm^{-1}) (Figure 3.17). Pb is identified, possibly as lead white, and a few red grains contain C and Al, likely associated to a red lake.

In the Pavia's altarpiece (P4) the artist painted a first light yellow layer containing Pb and Sn, identified by Raman as lead and tin yellow type I. On top of that, there is a second orange layer, and As and S are found; a broad Raman band at approximately 340 cm^{-1} identifies an amorphous arsenic sulfide, a second weaker band at 232 cm^{-1} could be related to realgar-like nano phases, indicating the use of the dry process in the making of the pigment [17–20] (Figure 3.18).

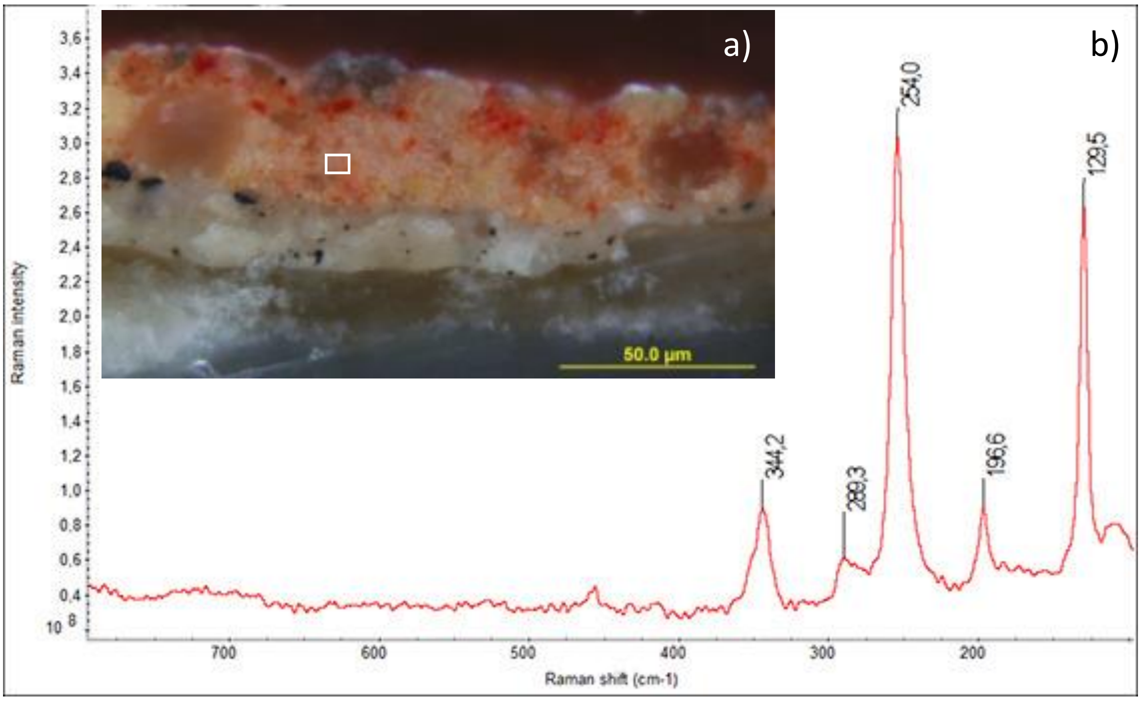


Figure 3.17. a) Cross section of the orange sample of P3; b) Raman spectrum collected on the orange layer (spot of analysis indicated by the white square).

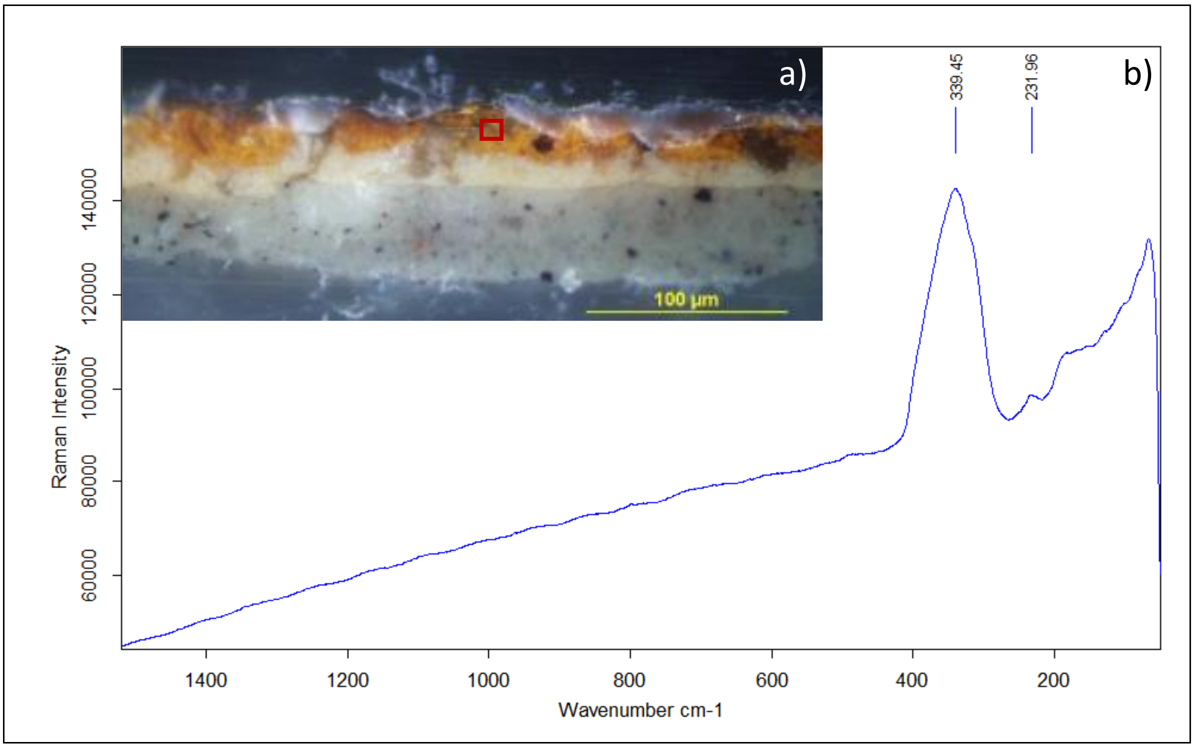


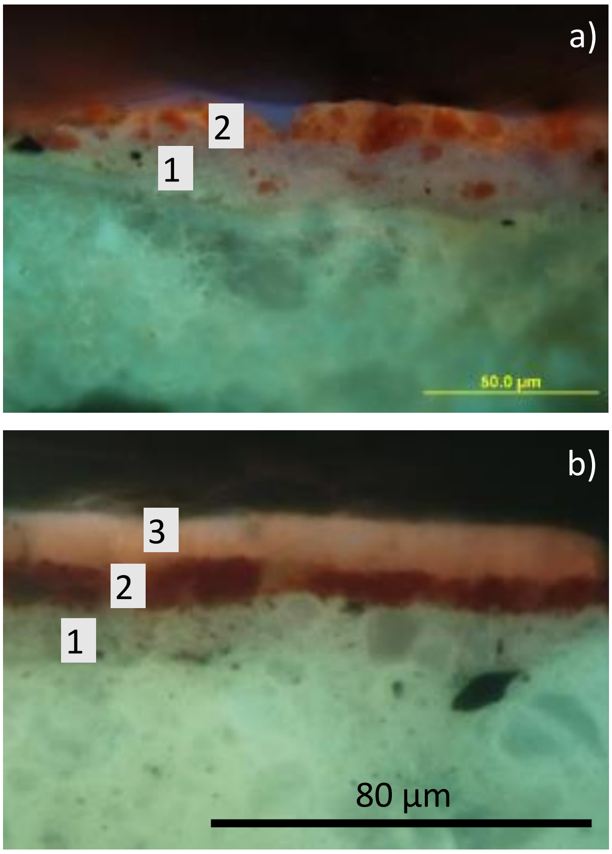
Figure 3.18. a) Cross section of the orange sample of P4; b) Raman spectrum collected on the orange layer (spot indicated by the red square). The broad band approximately at 340 cm^{-1} and the weak one at 232 cm^{-1} are associated to amorphous arsenic compounds.

Red pigments

Red areas are obtained through several overlapping pictorial layers and the technique does not seem to vary over time.

The structure of the red layers has been previously investigated by other researchers on the *Christ carrying the cross* (circa 1510-1530) and the *Salomé* (circa 1510-1530) of the National Gallery of London; in particular, in these two English artworks, in order to obtain an intense red, Gianpietrino spreads red lakes on a red-brown layer based on red earth, vermilion and black pigments [14]. In the lighter areas, as in the sleeve of the Salomé, he uses a more standard technique where the red lake is applied on a pink layer based on a mixture of white pigments and red lake. This latter technique is found in the red sample of Saint Catherine (P3). In particular, the first pink layer mainly consists of Pb, likely associated to lead white, and a few grains of C and Al are possibly linked to a red lake; this hypothesis is also corroborated to the intense pink UV fluorescence, characteristic of the organic lakes and dyes (Figure 3.19).

The Pavia’s altarpiece (P4), which has an intermediate degree of red colour on the Virgin's garment, shows a pictorial construction of three layers: one pinkish, one red-orange and finally the upper one red (Figure 3.19). The first pink layer mostly contains particles made of C, probably as carbon black, and Fe, likely red ochres; a few C and Al-based grains can also be associated to the presence of a red lake. FTIR absorptions at around 1400 and 838 cm^{-1} identify lead white. The second red layer contains mostly Hg, identified by Raman as vermilion, Fe-based grains, likely related to ochres, and C and Al-based particles, possibly related to a red lake. The final red layer contains only C and Al, and therefore it was made of red lake, showing also an intense pink UV fluorescence.



Analyses on the layers of the red sample of P3 and pigments identification.		
2	SEM-EDS: C, Al	Red lakes/dyes
1	SEM-EDS: C, Al, Si, Pb, Ca, Fe	Lead white, red lakes/dyes

Analyses on the layers of the red sample of P4 and pigments identification.		
3	SEM-EDS: C, Al	Red lakes
2	SEM-EDS: C, Al, Si, Hg, S, Ca, Fe Raman: 254, 285, 343	Vermilion, red ochres, red lakes
1	SEM-EDS: C, Mg, Al, Si, Pb, Ca, Fe FTIR: 2923, 2853, 1731 1395, 1050, 838	Lead white, red ochres, carbon black, red lakes

Figure 3.19. a) Cross-section of the red sample of P3, UV; the identification of the pigments are described in the table; b) cross-setion of the red sample of P4, UV; the identified pigments are expressed in the table.

Blue pigments

Blue areas are not painted on P1, therefore no sample was taken. The blue sample of the Virgin and Child (P2) shows two blue layers. The bottom one contains mostly Cu and Pb, likely to be azurite and lead white, respectively. The top and thinner one consists of Na, Si, Al, S, K, Ca, which are the elements typically related to lapis lazuli, while the weak peak of Pb is possibly associated to lead white (Figure 3.20).

Saint Catherine (P3)'s blue sample has a single pictorial layer, and the Raman microscopy identified bands at 401 and 1096 cm^{-1}, associated to azurite (Figure 3.21).

The Pavia's altarpiece's blue sample (P4) has a single thick layer of blue crystals identified by Raman as lapis lazuli (545, 1307 cm^{-1}) (Figure 3.21).

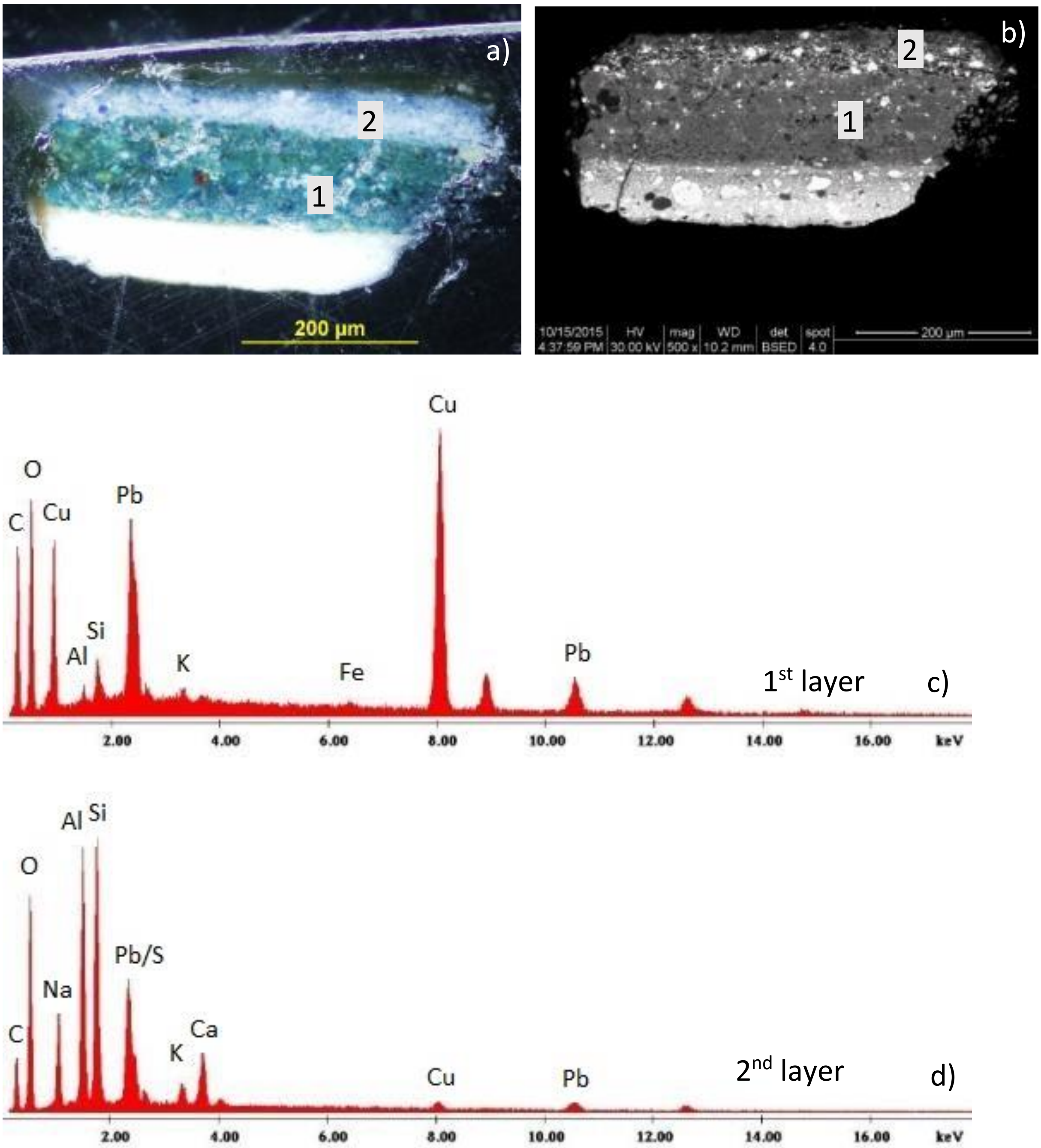


Figure 3.20. a) Cross-section of the blue sample of P2; b) SEM-BSE image; c) SEM-EDS spectrum collected on the first layer; Cu and Pb are probably associated to azurite and lead white; d) SEM-EDS spectrum collected on the upper layer, showing the characteristic elements of ultramarine (Na, Al, Si, S, K, Ca) and Pb as possibly lead white.

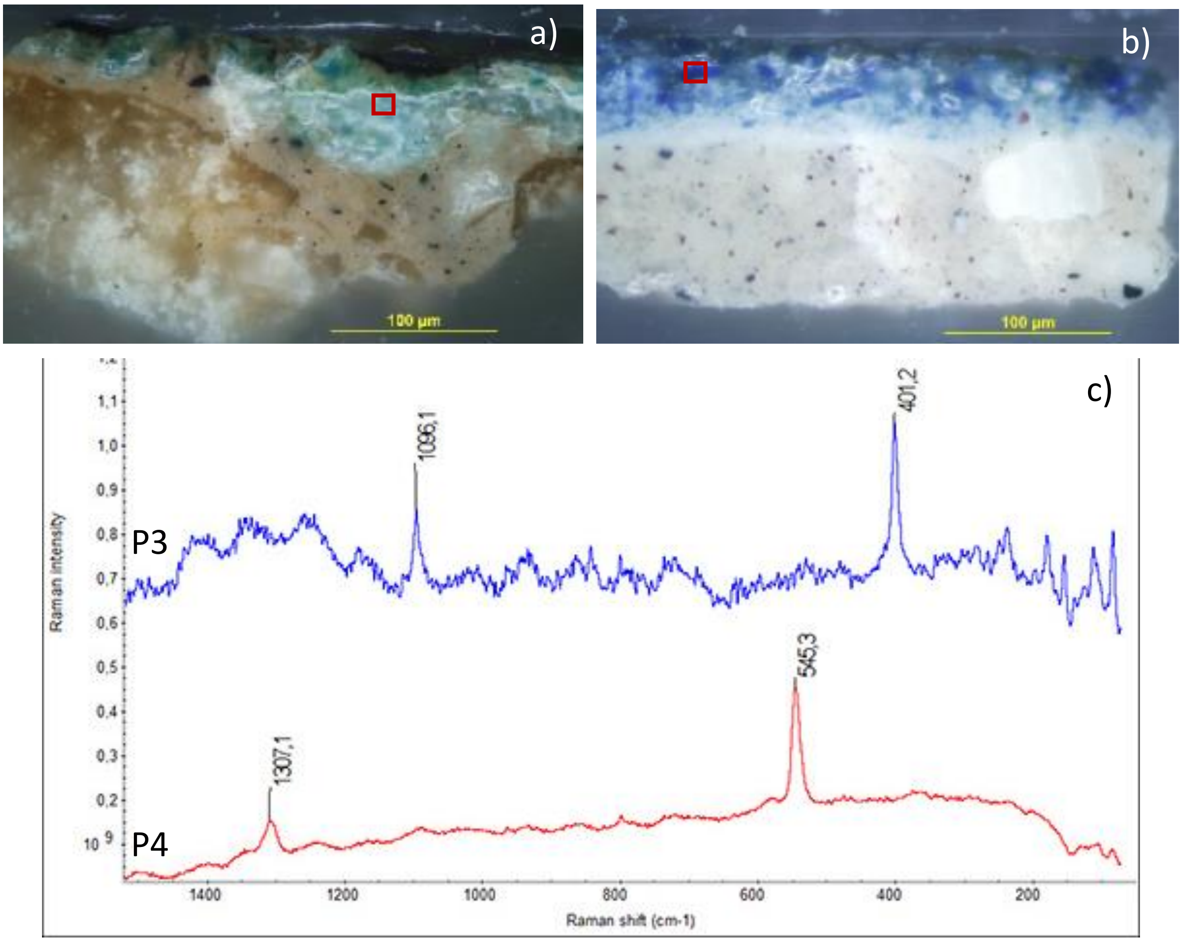
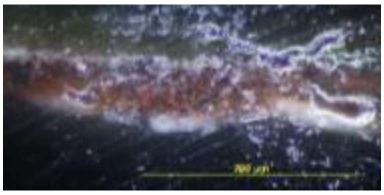
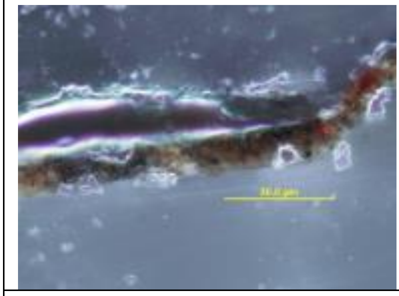


Figure 3.21. Cross-sections of a) P3 and b) P4; c) Raman spectra collected on the blue layers of these samples (spots indicated by red squares).

Flesh tones

The sample collected on the hand of Mary Madgalene (P1) is made of a first layer directly applied onto the ground. Particles of various colour are present: the Fe-based red/orange ones are likely made of ochres, Hg-based red ones are vermilion, as confirmed by Raman, and C-based black ones are possibly carbon black. Pb is likely associated to lead white, and FTIR analyses identified hydrocerussite (3537, 1399 cm^{-1}). The binder is identified as a drying oil, and the peak at 1708 cm^{-1} of the free fatty acids and the band at 1542 cm^{-1} of lead carboxylates indicate a degradation process. In order to make the shade darker, a second layer is applied on top of the first one, and it is enriched in C black particles. This technique is found in the Leonardo’s *Annunciation* (1475-1478) and *Belle Ferronnière* (1490-1495) [9].

In the Dutch painting (P2), manganese compounds are added to a single pictorial layer in order to darken the tone. Lead white, ochres, vermilion and carbon black are also suggested on the basis of SEM-EDS analyses. In this regard, it should be noted that, according to the study mentioned above, both the *Mona Lisa* (1503-1514) and *St. John the Baptist* (1506-1513) show an addition of manganese compounds in the shadowed flesh tones. Therefore, the first testimony in Leonardo's technique of the use of manganese compounds to obtain the shadows is around 1503. It could be suggested that Leonardo, returning to Milan in 1506, brought with him not only the new glaze technique, used in the *Mona Lisa*, but even new materials, such as the manganese compounds that Gianpietrino applies in the *Virgin with Child* (P2); this artist attempted to adopt the complex glaze technique of the Master only later, for instance this practise is attested in the *Christ carrying the cross* (1510-1530) [14].

Paintings	**Analytical results**		**Comparison to Leonardo's paintings**
P1 	SEM-EDS	2nd layer: C 1st layer: C, Ca, Pb, Fe	2nd layer made of C-based black pigments 1st layer: lead white, red and orange ochres and vermilion *Annunciation* (1475-1478); *Belle Ferronnière* (1490-1495)
	Raman	1350, 1585 (carbon black) 254, 285, 344 (vermilion)	
	FTIR	2929, 2857, 1730 (sh), 1708 (drying oil) 1542 (lead carboxylates) 3537, 1399 (lead white) 1044 (silicates)	
P2 	SEM-EDS	Al, Si, Pb, S, K, Ca, Mn, Fe, Hg	Mn compounds *Mona Lisa* (1503-1514); *St. John the Baptist* (1506-1513)
	Raman	-	
	FTIR	-	
P3 	SEM-EDS	C, Al, Si, Pb, Ca, Fe, (Cu), Hg	Carbon black, ochre, earth pigments *Saint Anne, the Virgin and the Child* (1510-13)
	Raman	254, 345 (vermilion)	
	FTIR	-	
P4 -	XRF: Ca, (Mn), Fe, Pb, (Cu)		

The sample of *Saint Catherine* (P3) consists of a single layer made of Pb and Fe, likely related to lead white and red ochres, respectively. A few particles based on C and Al are likely associated to red lakes, and red Hg-based particles are univocally identified by Raman as vermilion.

In the Pavia's altarpiece (P4), the shadowed area, analysed only by XRF, presents mainly Pb, likely associated to lead white, and Fe, possibly indicating the use of ochres, but also earth and umber pigments considering the small amount of Mn. The presence of C-based black pigments is suggested. Leonardo's *Saint Anne, the Virgin and the Child* (1510-13) shows a similar composition, as the shadows are made with translucent glazes or opaque pigments based on carbon black, ochre and earth pigments [9].

In conclusion, the investigation of the shading techniques on flesh tones suggests an evolution of the artist's technique over time and a close relationship with Leonardo.

3.2.4 Conclusion

Despite the current debate among art historians on the chronology of Gianpietrino's early works, scientific studies on the works of this artist are lacking.

In this study, the proposed sequence of analytical techniques has gathered information about the artist's palette, which consisted mainly of common pigments mixed with an oily binder and widely spread in the 16th century. This methodology has also permitted characterisation of the technique of execution, a possible evolution over time and the condition of the objects; the comparison with Leonardo's technique for the flesh tones underlines the close relationship between pupil and Master and allows understanding of how Gianpietrino imitated and partly reworked Leonardo's teachings.

The four paintings are primarily differentiated on the basis of the colour and location of the *imprimitura* and the rendering of the shadows in the flesh tones (Figure 3.22).

In the case of the *Saint Mary Magdalene* (P1), the white priming present only under the green areas and the shaded flesh tones, obtained with the application of a second pictorial layer based on carbon black, are information that allow to date the artwork to the first decade of the 16th century, placing this painting among the early works of Gianpietrino. In addition, the green area of the dress obtained without the application of a final glaze layer, a technique requiring a certain artistic ability that Gianpietrino only masters at a later time, and the yellow achieved with ochres, and not with lead and tin yellow and arsenic compounds that he will use later, corroborate the hypothesis that it is a work of the first period of the artist. Moreover, the presence of the sarcophagus, an element not common in the representations of Mary Magdalene, which covers an already painted portion of the artwork may suggest a non-optimal rendering of the left hand of the saint or a request due to the taste of the client. Finally, the study on the jar by IR reflectography has shown that at least three drawings can be recognised below the final one. For this reason, the painting has been identified as a prototype of a series of paintings that evidently at that time received some success.

The *Virgin and Child* of the Rijksmuseum of Amsterdam (P2), dated around 1510, differs from *Mary Magdalene* (P1) due to the presence of manganese-based compounds in the shadowed flesh tone, possibly used after Leonardo’s return to Milan in 1506. The underlying painting, as shown by X-ray radiography, demonstrate how the artist initially painted a standard position of the Virgin’s face, similar to Mary Magdalene’s face, but then he chose to replace it later with a slightly tilted position, providing a level of movement, and possibly liveliness, to the painting.

Martyrdom of Saint Catherine (P3) shows a grey priming, similar to the two paintings of the National Gallery of London (both dated 1510-30). The absence of manganese in the shadowed flesh tones and the presence of lead tin yellow may suggest a date range after 1510 and possibly up to 1530. Further investigations on other paintings dated to this period could help in distinguishing whether P3 was painted before or after P4.

Madonna with Child between Saint Jerome and Saint John, the Pavia’s altarpiece (P4) dated 1521, presents the same grey priming of P3 and, in general, a more complex stratigraphy, greater attention in the colour rendering and prevalent and sometimes extensive use of precious pigments.

This study has therefore allowed characterisation of the materials of four paintings made by Gianpietrino and his technical evolution over time, and succeeded in determining a few characteristics useful for the identification of a Gianpietrino painting. The dating range of two paintings was also better defined based on of scientific results. This could help in further studies for attribution as, as previously stated, his name has been used as a sort of container for a wide number of artworks referable also to collaborators and followers.

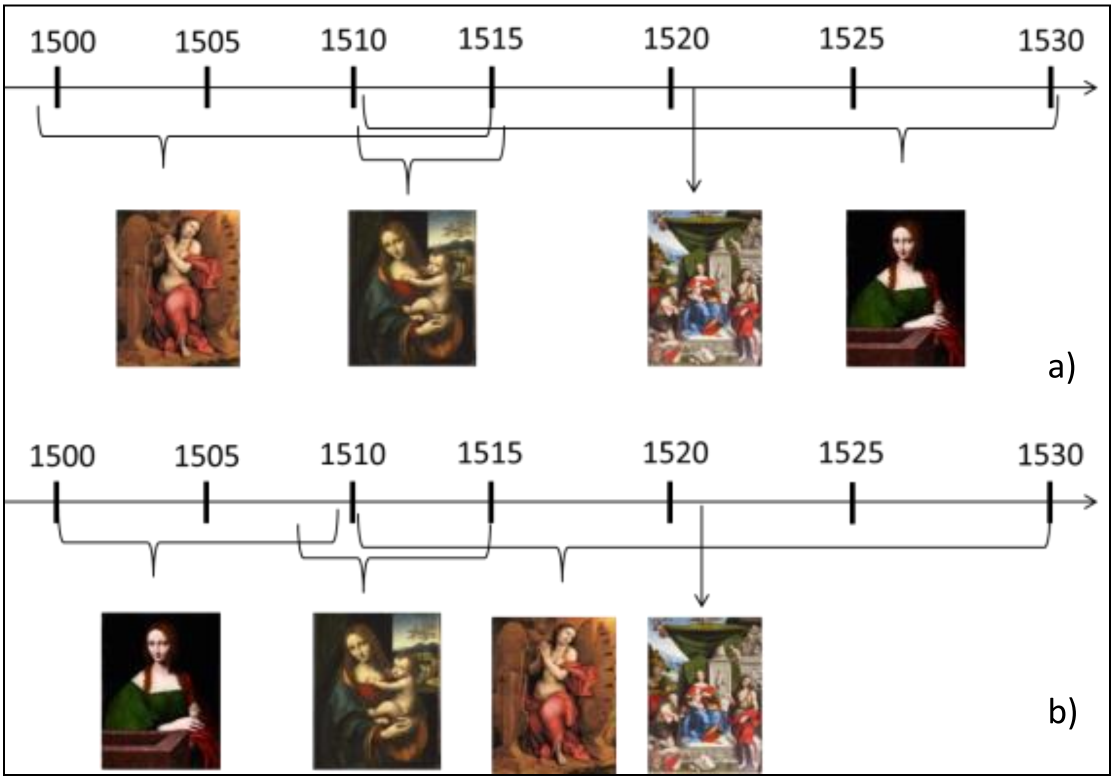


Figure 3.22. a) Timeline of the four Gianpietrino’s paintings, based on stylistic evaluation; b) timeline after the results of scientific analyses.

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Chapter 4

Paintings with documentation and distinctive markings

4 Paintings with documentation and distinctive markings

The potential presence of inscriptions, signatures and/or markings applied on a painting deserves to be documented and evaluated, as these features provide initial information on the object and therefore hint at an attribution. Through visual examination of the front and reverse, a first insight about a suggested artist or period of time or collection could be gathered.

Given that this kind of documentation tends to add value to the painting and therefore confirm the attribution, it should be carefully evaluated to detect misleading information.

In addition, every kind of written documentation referring to the object should be also taken into consideration, for instance, the research of the provenance and the investigation of auction houses' catalogues and archives. This kind of study is carried out by other professionals, such as art historians and conservators, therefore a discussion on this aspect lies beyond the scope of this research.

In this section, inscriptions on the back of the painting and signatures on the front side are taken into account, and examples of their investigations are described.

4.1 Inscriptions on the back of the painting

When possible, the documentation of the back of the paintings is of extremely importance, not only for the investigation of how the artwork was constructed and the original format and function, but also due to the possible presence of inscriptions and markings, such as seals and numbers likely related to a collection or associated to an auction house or an archive. It is necessary to establish if the information on the back is an original part of the painting or a later addition. The latter opens the path to a possible examination of further aspects, such as a documentary research and the painting's materials, in order to understand if it is a fraudulent action or a misinterpretation of the object.

For instance, the name of an artist, a dating and a location can be present, and therefore these features need to be investigated. The painting *Angel holding a tabula ansata* is an example of such a case and the findings will be disclosed below.

A graphological examination carried out by an expert could be useful to identify the type of calligraphy, which can indicate a particular period.

When the name of an artist is present, a further step consists of documentary research on the artist in question, which can help to find artworks with the same subject. In the case of minor artists, this kind of research is not always possible, in the case of the painting *Paysage de montagne*, described in the following section, and other solutions should be found.

Tracking the movements of the artist during his/her lifetime can also be useful to check a possible correspondence between the year and location, whether or not indicated on the painting.

Finally, the use of scientific analyses provides essential evidence about the materials used on the artwork. Thus, comparing technical results with the documentation written on the back, for example the date, the geographical setting and the name of the artist, new information is furnished which better contextualises the object.

4.1.1 Angel with a *tabula ansata*

Introduction

The back of the panel *Angel holding a tabula ansata* (private collection, image not shown) shows the following inscription: "A. D. 1764 A. R. M. fc. Roma", that is "Anno Domini 1764 Anton Raphael Mengs fecit Roma" (Figure 4.1). In this view, the painting is attributed to the German artist Anton Raphael Mengs (1728-1779), a Flemish artist who copied the Old Masters of the Italian Renaissance [1]. In this specific case, a date, a location and the name of an artist are present and need to be checked in order to understand and classify the type of object under study.

Figure 4.1. Inscription on the back of the painting.

Documentary research

Given the presence of an artist's name, an art historical research on Mengs was carried out in order to define his movements in Italy, and especially his presence in Rome during the year 1764.

Although the inscription suggested 1764 as the painting's year of execution and Rome as place, in that year Mengs was in Spain at the Royal Court [2], indicating a first clue about a misleading information. In addition, the painting under study depicting an angel is clearly a copy of the well-known *Virgin with Child and Saint Francis, Saint John Baptist, Saint Jerome and the donor*, better known as “Madonna of Foligno”, made by Raffaello Sanzio. This altarpiece is preserved in Foligno, city that Mengs did not visit during his stay in Italy, making it difficult for him to have the chance to specifically copy this painting.

Therefore, the inscription is not correct and erroneously added to the painting at a later time. However, the hypothesis of a genuine misattribution cannot be ruled out: the painting can be an original, possibly made by some other artist as Mengs never visited Foligno and thus did not have access to the Raffaello’s painting. Thus, the location, Rome, and the 1764 year can still be possibly accurate.

In order to evaluate if the suggested year is compatible with the painting’s materials, the object should be treated as a painting presenting a chronological attribution. Analysing the materials estimates therefore a time range of execution and it can possibly help in understanding if the inscription on the back is genuinely or fraudulently added.

4.1.2 Paysage de montagne

The painting *Paysage de montagne* (see image in section 5.1) shows the name of the artist, Jan Ruyscher, on the back; the writing is especially highlighted under UV (Figure 4.2). In this case, no year or place was indicated, therefore no documentary research could be carried out. In addition, no signatures of this artist were available so to compare the writings to the one under study.

In order to evaluate if the writing was authentic or forged, the only option was the study of the artwork’s materials and technique. The few information available about this Dutch painter were also combined with the scientific results in order to determine the authenticity. The artwork thus becomes a painting with an attribution to an artist (see section 5.1).

Figure 4.2. Inscription on the back of the panel with the name of the artist, under UV.

4.2 The presence of a signature

The presence of a signature, which is an element favouring the attribution, and thus adding value to an artwork, needs to be carefully evaluated as it can be easily forged. A signature is usually present on the front of the painting, in one of the corners, and is the final touch on the painting, sometimes applied after the varnish.

4.2.1 Graphological examination

A non-invasive way to analyse the signature is by performing a graphological examination and comparison between the object under study with other paintings of clear originality; in this way similarities and differences can be evaluated. This type of examination is possible in the case of well-known and modern artists, but for minor and historic ones it is not easy to find signatures for a comparison. The use of technical imaging can help in the identification of features not entirely visible in visible light.

For instance, the signature on a painting allegedly by Renoir (image not shown) was studied[12] (Figure 4.3). A series of signatures on verified Renoir paintings from 1875 to 1914 were examined (Table 4.1), comparisons between the writing revealing differences which provided an indication that the painting under study is likely not to be an original. The most relevant differences present in the studied signature are the general straightness of the letters, without the customary pronounced slant, and the absence of the dot after the artist's name. The round shape of the R at the left side, the attachment of the I to the letters before and the absence in the last R of the characteristic final curvature going down, compared to the line where the other letters are written, are also small details that differentiate the signature of the painting in question.

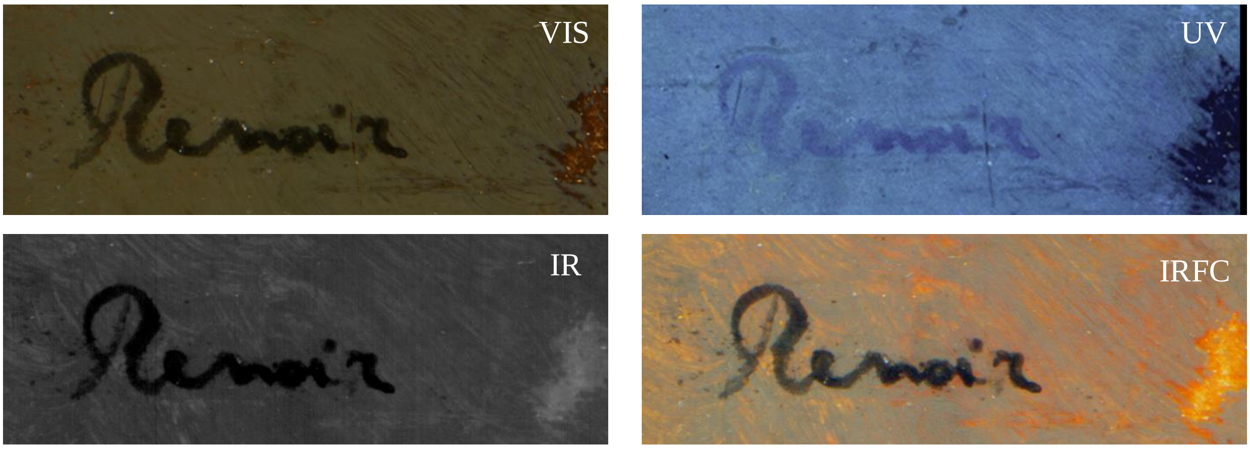

Figure 4.3. Technical imaging of the Renoir signature under study.

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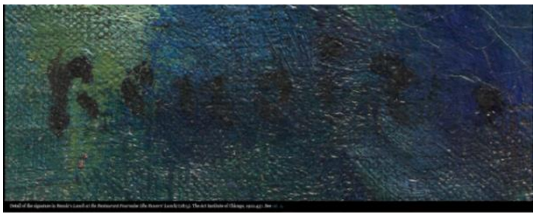
[12] Salvatore Andrea Apicella is acknowledged for his work on the Renoir's signature.

Table 4.1. Signatures made by Renoir on authentic paintings (© https://www.artic.edu/artists/36351/pierre-auguste-renoir).


Woman at the piano (1875-1876)


Lunch at the Restaurant Fournaise (1875)


Alfred Sisley (1876)


The Laundress (1877-1879)


Near the lake (1879-1880)


Acrobats at the cirque Fernando (1879)


Seascape (1879)


Near the lake (1879-1880)


Chrysanthemums (1881-1882)


Two Sisters (1881)


Madame Léon Clapisson (1883)


Lucie Berard (1883)


Girl with a Hoop (1885)


Julie Manet (1887)


Jean Renoir Sewing (1899-1900)


Seated Bather (1914)

4.2.2 Non-invasive analyses on the signature

Examination of the signature and the surrounding area under UV complements the investigation, as this technique can supply information related to the originality of the writing (Figure 4.4). For instance, UV can highlight a different fluorescence only from the signature, as in the case of the Renoir writing, or point out thick layers of varnish applied at a later date that prevent an easy reading of the writing (Figure 4.4a-b).

The UV fluorescence of a painting with a Munch signature (see image in Appendix A.02) provides a different response from the area where the signature was applied compared to the rest of the painting, due to retouching at the bottom of the painting (Figure 4.4c). In this case, it appears evident that the signature is written on top of a restored area and therefore the attribution of the whole object is reconsidered.

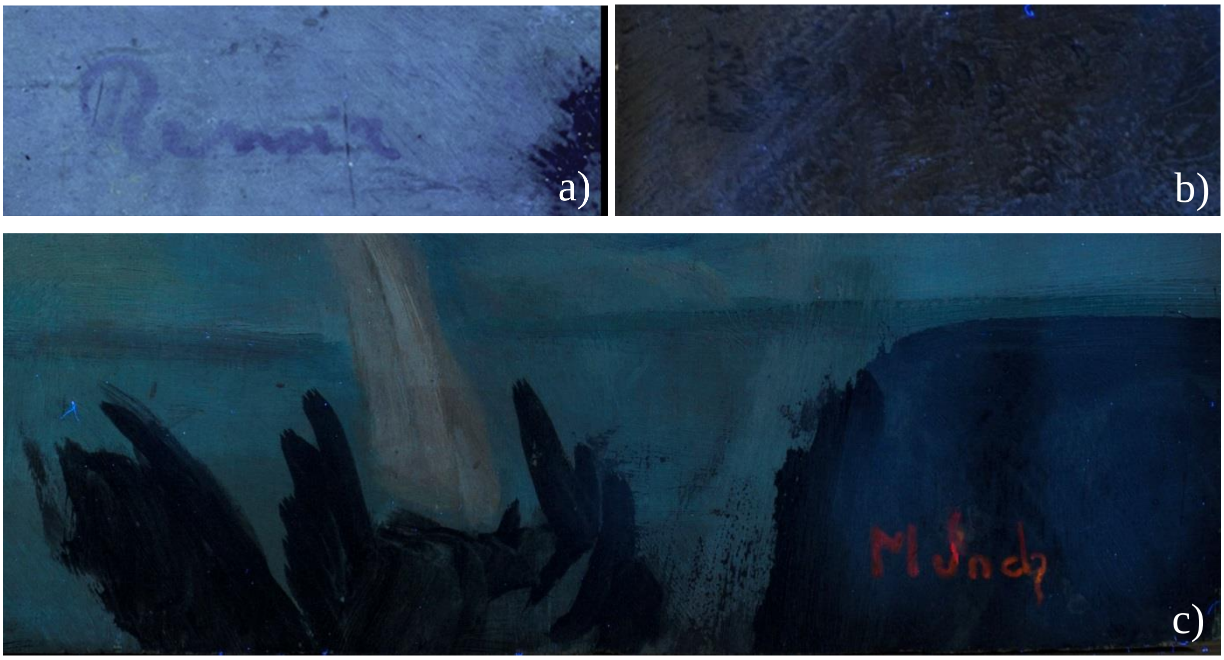


Figure 4.4. Signatures under UV, a) the UV underlines a different fluorescence from the signature in comparison to the background, b) thick varnish layers affect the readability of the signature, c) the signature is applied on a retouched area.

4.2.3 Micro-invasive analyses

A primary concern is understanding if the signature is contemporary to the rest of the painting or applied at a second point, as that can hint at a possible fraudulent intention. Although sampling from a signature should not be considered an option, as it is highly invasive, in a few cases it is the only option to confirm the authenticity of a painting. The case of the Rembrandt self-portrait studied at the Hamilton Kerr Institute in Cambridge in 2014 is an example: doubts about its authenticity were raised since 1968, but a detailed study of the painting's materials and technique and especially the cross-section obtained on the signature allowed corroboration of the authenticity of the object[13].

In the case of the Munch painting (Appendix A.02), the signature is written above a rectangular retouched area at the bottom right. In order to understand when the retouch was made in comparison to the rest of the painting, and thus validate if it was still compatible with Munch's lifetime, it was decided to take a sample from an area near the signature. In this way information were collected about the area where the signature was, without touching directly the brushstrokes of the writing[14].

The obtained cross-section (Figure 4.5, Table 4.2) consists of a first green layer (nr. 1) laid directly on top of the support. The results of SEM-EDS show zinc as the main element, possibly associated to zinc white, and a very small amount of other elements, among which cadmium, possibly associated to cadmium yellow, chromium, probably as chrome oxide, and barium, likely as barium sulfate (Figure 4.6). Raman microscopy identifies PG7 (*Color Index Generic Name* Pigment Green 7, *Colour Index Number* 74260, copper polychloro phthalocyanine) and vermilion. A thin organic layer (nr. 2) is applied on top and then a blue layer is observed (nr. 3), clearly added at a second time.

Interesting results were also obtained on this superficial blue layer. SEM-EDS results show calcium and titanium as the main elements, with small amounts of zinc, iron, phosphorus (Figure 4.6), possibly linked to zinc white, Fe oxides and bone black, respectively. Moreover, Raman microscopy identifies calcium carbonate, Prussian blue, ultramarine blue, PG7 and titanium white in the rutile form (Figure 4.7). The main presence of titanium white as white pigment, the absence of barium sulfate, substituted by calcium carbonate, the coarse granulometry of the blue pigment,

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[13] https://www.theguardian.com/artanddesign/2014/jun/10/disputed-rembrandt-is-genuine (accessed on August 2019); https://www.nationaltrust.org.uk/buckland-abbey-garden-and-estate/features/uncovering-a-masterpiece (accessed on August 2019); https://www.ntsouthwest.co.uk/2014/06/old-master-selfie-is-a-rembrandt-2/ (accessed on August 2019).

[14] This paragraph is partly published in Fiorillo F. *et al.*, *A multi-analytical approach for the characterisation of 20th century paintings*, 2019, Eur. Phys. J. Plus, 134: 373. DOI: 10.1140/epjp/i2019-12752-5.

the different UV fluorescence in this area, the presence of an organic layer underneath the final blue layer corroborate the hypothesis that this layer was added at a later time.

Concerning the original layer (nr. 1), the finding of PG7, commercialised since 1936 [3], gives a *post quem* date of the artwork, thus opening the possibility of a Munch's late period painting (1936-1944, year of Munch's death) or a copy in the manner of Munch after 1936. The presence of titanium white in the rutile form, widely used in Europe since 1945 [4], indicates that the layer containing the signature was laid after Munch's death in 1944. However, the materials identified in the original areas of the painting (see Appendix A.02) are fully compatible with Munch's lifetime, raising different hypotheses about the nature of this artwork. For instance, the painting can be an unknown painting made in the 20th century, possibly in the manner of Munch, and then misattributed to Munch (genuinely or not) due to the presence of the signature. Or it can actually be an original painting, retouched at the bottom due to conservation issues; the signature applied at a later time seems a fraudulent element, but a genuine misattribution or a retouching of a previous signature cannot be ruled out.

Finally, it cannot be discerned if the painting is an original or if it is a copy in the manner of Munch, with the later addition of the signature (as a genuine or fraudulent misattribution), because no data are published about materials of this artist's late period.

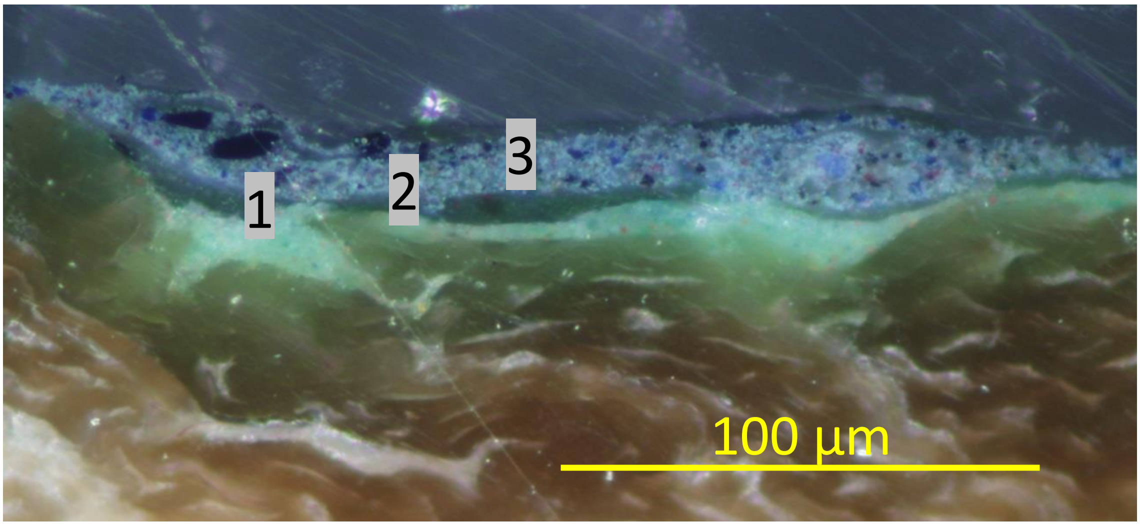

Figure 4.5. Cross-sections in visible light, blue sample near the signature. The layers are numbered and the results of SEM-EDS and Raman analyses are expressed in Table 4.2.

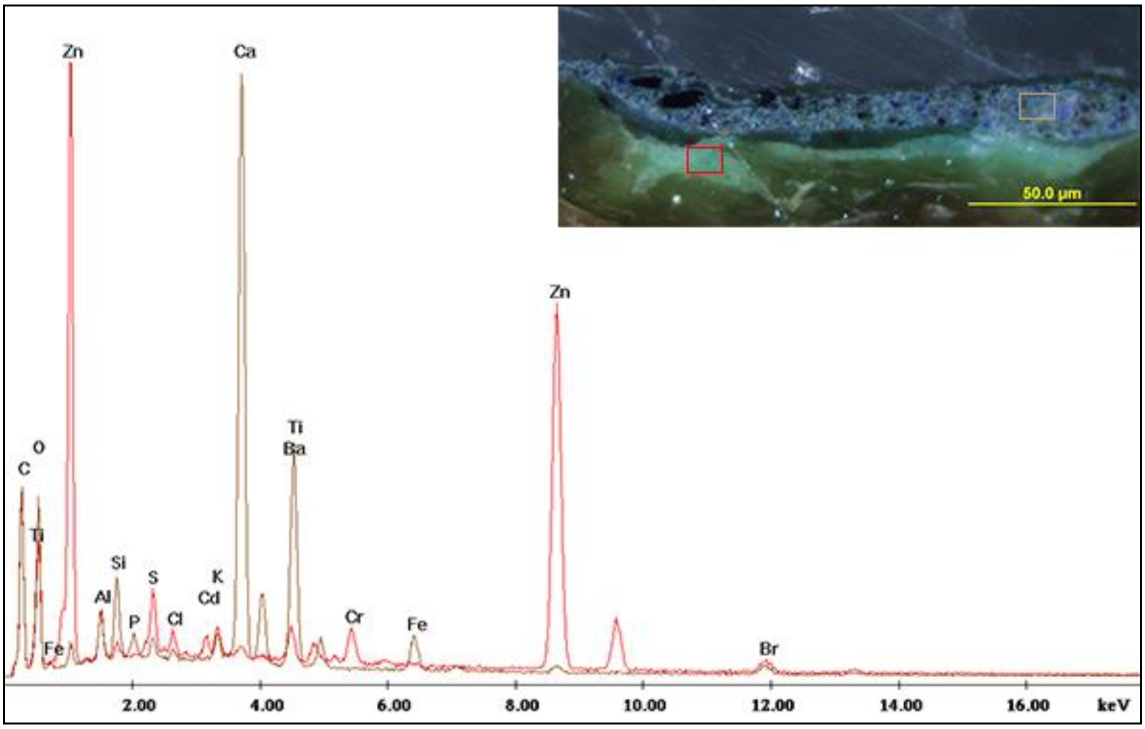

Figure 4.6. SEM-EDS spectra collected on the blue layer (brown trace) and on the green layer (red trace) of BW3. In the cross-section image the areas analysed are indicated in squares.

Table 4.2. The results of SEM-EDS and Raman analysis on the cross-section are described, along with their possible interpretation.

Nr.	SEM-EDS	Raman (cm^{-1})	Pigment interpretation and chemical composition
3	Al, Si, P, S, Ca, Fe, Zn	2152, 2090 (Prussian blue) 1330, 1660 (amorphous carbon) 443, 612 (titanium white, rutile) 1086 (calcium carbonate) 1528, 1342, 748 (PG7)	Calcium carbonate ($CaCO_3$) Titanium white, rutile (TiO_2) Prussian blue ($Fe_4[Fe(CN)_6]_3$) Bone black (Ca phosphate) Carbon-based black Zinc white (ZnO) Fe oxides Phthalocyanine green, PG7
2			Organic material
1	C, Al, Si, S, Cl, Cd, Ba, Cr, Zn	1535, 1339, 1289, 1214, 777, 741, 686, 255 (PG7) 255, 340 (vermilion)	Zinc white (ZnO) Barium sulfate ($BaSO_4$) Lithopone ($BaSO_4$, ZnS)? Calcium carbonate ($CaCO_3$) Phthalocyanine green, PG7 Chrome-based green (Cr oxides) Cadmium sulfide (CdS) Vermilion (HgS)

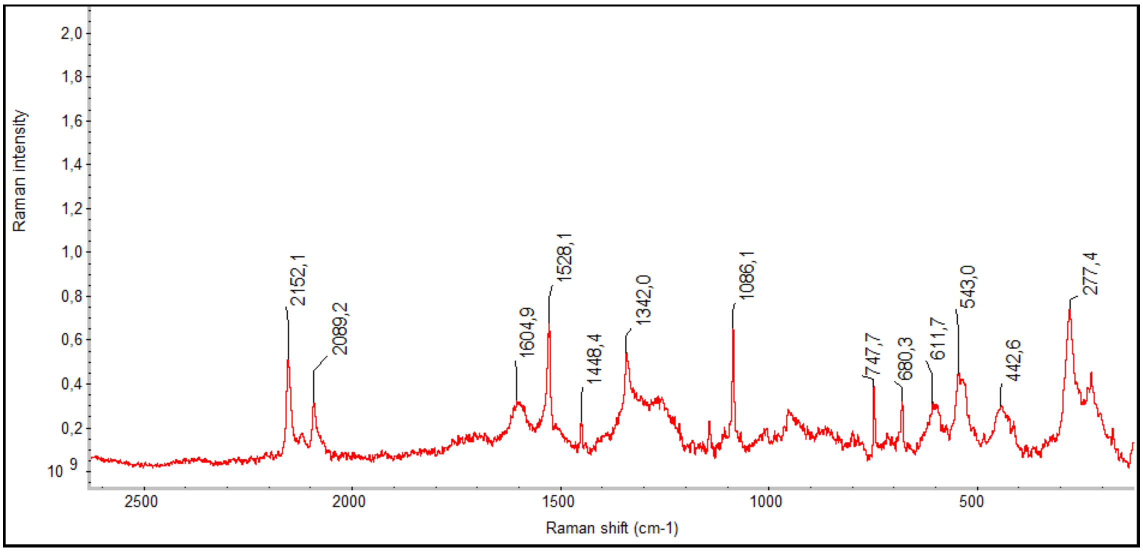

Figure 4.7. Raman spectrum of the blue layer (nr. 3) of BW3. The identified pigments are Prussian blue (2152, 2089, 277 cm^{-1}), PG7 (1528, 1342, 748 cm^{-1}), calcite (1086 cm^{-1}), titanium white, rutile (612, 443 cm^{-1}) and ultramarine blue (543 cm^{-1}).

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Summary tables

INSCRIPTIONS ON THE BACK OF A PAINTING			
Artist's name	**Artist's name + date and/or location**	**Date (and location)**	**Seals / inventory number**
Documentary research to possibly find similar subjects on other paintings	Documentary research to check compatibility with the artist's lifetime and/or location: 1. The inscription is contemporary to the painting and add value to the object 2. The inscription can be applied at a later time: - genuine or fraudulent misattribution	Materials characterisation to check compatibility with the suggested date (and location)	Documentary research on the type of inscription, re-trailing the history of the painting
The object becomes a painting with an attribution (to an artist)		The object becomes a painting with an attribution (chronological and/or geographical)	

INVESTIGATION OF THE SIGNATURE			
Methodology		**Notes**	**Possible gathered information**
1	Graphological examination	Comparison with signatures of authentic paintings, if available	Corroboration or not of the suggested attribution
2	Non-invasive analysis: UV	The signature does not show UV fluorescence	It is possibly contemporary of the painting (original/replica/copy/fake)
		The signature is covered by thick layers of varnish and it cannot be investigated	
		The signature shows a diverse UV fluorescence in comparison to the rest of the painting	Applied later by the same artist (retouching) or not (counterfeiting)
3	Micro-invasive analysis: sampling	Not directly non the signature, but in a nearby area (if possible)	Information on original and retouched layers

Chapter 5

Paintings with an attribution

5 Paintings with an attribution

Attribution, as defined by the National Gallery of London, is the "assessment of who was responsible for creating a particular work", and, interestingly, it is stated that it is made with varying degrees of certainty, depending on the stylistic study, documentary evidence and scientific research. A research based on style and documentary evidence offers valuable information as to a timeframe and possibly a geographical setting, but proposing a probable author or a school is not always allowed. In this case, the attribution is made to a general chronological range and geographical context (i.e. "16th century Tuscan area" or "17th century French school").

Scientific analyses help in corroborating or disproving arguments related to an attribution, as some materials are specific to a particular period and possibly, an artist.

Investigation of the suggested period of time

To confirm or disprove the suggested attribution, the first step of a scientific protocol should be the use of non-invasive analyses to assess the state of preservation and check the compatibility of the materials with the suggested period. In fact, whether a chronological period, such a particular century, or an artist, who lived in a specific time, is proposed, the actual period can be checked, as a painting's materials are produced in specific times and thus the dating range can be compared to the one of the painting/artist in question.

After thorough documentation of the artwork with multispectral imaging in order to establish retouched areas, pigments are commonly identified by non-invasive analyses, such as XRF. If the results are compatible with the chronological attribution, further micro-invasive analyses can conclusively characterise the materials (pigments and binders), to define every compound and localise it in the paint layers. At the end, a comprehensive characterisation of the object in terms of materials and technique allows assessment of the compatibility with the attribution with a higher degree of certainty while at the same time some aspects, such as dating and geographical location, can also be narrowed down. In addition, the gathered information about the object can be used for future studies on similar objects, belonging to the same time or to the same artist.

Results of non-invasive analyses can also hint at a non-compatibility of the object with the chronological attribution. The case of the painting *Paysage de montagne* and attributed to the Dutch artist Jan Ruyscher is an example of such a case (see paragraph 5.1). Ruyscher lived in the 17th century, probably between 1625 and 1675. This painting was sold by an auction house in 2014;

dendrochronological analysis on the support, based on the counting and pattern of tree rings, indicated 1660-1740 as timeframe. Due to the questions around this analysis, a new and further study was carried out to determine the type of object. Following investigation under UV and the consequent avoidance of retouched areas, XRF analyses showed the presence of elements associated with 19th and 20th century pigments. In particular, titanium, likely linked to titanium white, was widely identified across the whole surface, appearing to infer that the artwork was painted at least in the 1920s, as this is the date of commercialisation of the pigment. Further analyses of cross-sections will better clarify the pigments used and classify the object, but non-invasive analysis, such as multispectral imaging (UV fluorescence) and XRF, identified an incompatibility of the painting with the suggested artist's lifetime.

In the case of incompatibility of the results with the suggested attribution, such in this case, the artwork falls into the category of "Unknown artworks". A re-assessment can be made to identify the type of object.

On the other hand, following non-invasive analyses that established compatibility with the chronological attribution, carrying out micro-invasive analyses offers different scenarios.

The dating proposed by the attribution should be checked on a micro-scale, and in the case of compatibility, further aspects should be analysed to determine if the object is an original, a contemporary copy or a replica.

The painting *Mon Amour* from a private collection, attributed to Pablo Picasso, shows a very common subject among Picasso's paintings between 1911 and 1916 - a still life with musical instruments. The painting, which has Picasso's signature on the top left side, was hypothesised to be from around 1915 by stylistic evaluation. After non-invasive and micro-invasive analyses, a dating fitting the findings was identified and the artwork was dated from 1905 to the present, due to the identification of PR3, a synthetic colourant in commercial production since 1905, thus establishing a possible compatibility with the lifetime of Picasso (1881-1973) (see paragraph 5.2).

However, the detection of some features may entirely or slightly alter the suggested attribution, which will thus be reconsidered.

The *Angel with a tabula ansata* (see paragraph 5.3), already discussed with regards to the investigation of the inscription on the back, is an example. The analysis of the ground (see Appendix B), which consisted mostly of lead white, allowed determination of the timeframe in which the painting could have been made from the second half of the 18th century to the 20th century. Integration of the information with pigment analysis narrowed down the timeframe, suggesting 1780s-1850 as the possible period of execution. The inscription on the back indicates Mengs as the artist of this painting, but his lifetime (1728- 1779) does not match the chronological range identified by materials characterisation.

Investigation of the geographical context

In the case of antique paintings in particular, a geographical context is usually expressed together with a chronological attribution. Investigating the materials present in the painting and interpreting the results in conjunction with an accurate study of literature pinpoints diverse locations from which the artwork could have been made.

A case study discussing this aspect is described below (see paragraph 5.4). The painting *Columbine* was sold by Christies' as "Follower of Leonardo da Vinci, 16th century". Non-invasive analyses identified pigments compatible with the chronological time suggested by the attribution, however, cross-section analyses identified a ground layer based on calcium carbonate, which is characteristic of Northern Europe rather than Italy, where calcium sulfate was widely used in that period. Moreover, art historical research identified a very similar painting by Francesco Melzi, one of Leonardo's pupil. This piece of information allowed relation of the studied painting to Melzi and not directly to Leonardo. In conclusion, the object is still considered to be made by a follower, but based on Francesco Melzi's painting and not Leonardo's; the dating could be slightly moved between the end of the 16th and the beginning of the 17th century, and the geographical setting is Northern Europe and not Italy, probably France as Melzi remained there after Leonardo's death.

Micro-invasive analyses were thus fundamental in adding useful information to this object's history and to classify it as a copy with a specific timeframe and geographical context.

Investigation of the suggested artist

When the evaluation of a painting attributed to an artist needs to be carried out, a further step is the comparison of the results with artworks of the specific artist; accessible databases are of utter importance at this stage to achieve a reasonable consistency with the proposed attribution, and thus aim to ascertain the authenticity of the artwork. To further complicate this aspect, during their lifetimes artists experience a technical evolution leading to different technical choices - this is more evident starting from the 19th century. Therefore, artworks attributed to an artist in a specific period are essential sources of information, especially for 19th – 20th century paintings, as they provide useful findings to enlarge and inform databases. A case study of a 20th century painting is proposed to illustrate this aspect (see paragraph 5.2).

The 20th century is characterised by the employment of a wide variety of materials (organic and inorganic, natural and synthetic) by painters, along with a continuous development of their painting techniques. In addition, the spreading of fakes and forgeries in the art market makes the ascertainment of authenticity a significant challenge. If one single negative result invalidates the attribution, for example detecting anachronistic pigments, a single positive evidence of compatibility with the presumed period or artist needs to be carefully evaluated because it does not always make the authentication decisive. However, finding positive evidence (in this case the material's compatibility with an artist's lifetime) is the first step towards the determination of an unknown paintings' authenticity, even if the comparison of the results with published data is the only objective and significant way to ascertain their originality.

The materials characterisation of the painting *Mon Amour*, previously described, identified a date range from 1903 to the present for the execution of this painting, thus establishing compatibility with stylistic studies, which proposed around 1915 as a chronological attribution. This artwork was then further investigated in order to check the compatibility with Picasso's technique. Therefore, materials and technique used by the artist on original artworks were defined to the best of my knowledge, based on published literature. Although corroborated by a stylistic evaluation, in this case, the attribution to Picasso cannot be confirmed because no information is available about his materials and technique around 1915. Lack of published data prevented the classification of this object and the study is therefore not complete.

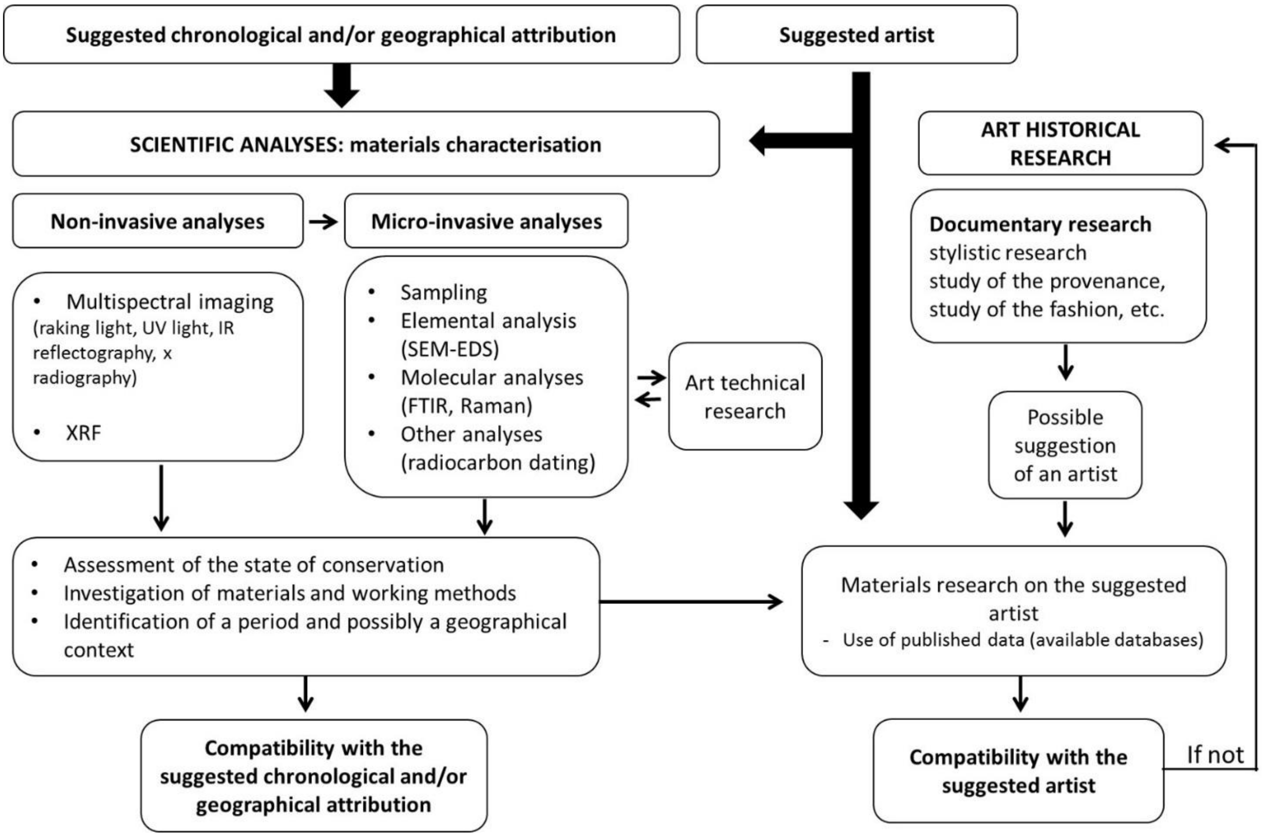
The thorough importance of the reconstruction of an artist's palette and technique is undeniable especially for 20th century art, when a great variety of materials, and ceaseless evolution over time, are accomplished. Sharing the results on original paintings should be strongly encouraged, as creating artists' databases is an essential step in the process of determining the originality of antique and modern paintings.

The suggestion of an artist

Scientific findings progress from answering general and perhaps more simple questions, such as the detection of a chronological context, to more specific ones, for example the confirmation of an artist to which to attribute a painting. This requires the combination of diverse techniques and skills to disclose new information and not only properly situate an artwork in a defined period and in a geographical setting, but also establishing a positive relationship between a painting and an artist.

The final step of the methodology is thus represented by the suggestion of an artist to whom a painting is attributed. This further step is advised for artworks with a suggested chronological and geographical context, which were analysed with various techniques and found compatible with the attribution. At the same time, if artworks were attributed to an artist and after technical investigation were found not to be compatible with the alleged artist, the focus of the research can be redirected to the suggestion of a new name, and thus the same further steps can be taken.

In an attempt to propose a possible artist, a stylistic study and therefore the integration and close collaboration with other professionals, such as art historians and conservators, is fundamental in order to reach a higher depth of investigation. The suggestion of a possible artist's name should also be evaluated from a scientific point of view, as in the previous step (investigation of the suggested artist), comparing the results with edited data and ideally enduring this cycle of proposing a name and testing it until finding a match.



Multiple attributions

The debates among diverse professionals over which artist painted a specific artwork or in which timeframe of his/her life an artist executed an object result in a rather controversial situation where a general agreement is not easily reached.

In order to pinpoint the execution of a painting to a specific timeframe during an artist's life, the characteristics of the suggested artist in terms of materials and techniques should be exhaustively examined, understanding the evolution over time and thus where to situate the analysed painting. In a more complicated situation, if a painting is attributed to different artists, each artist should be properly investigated, therefore the creation of ever-growing and accessible databases which comprise the complete information regarding each specific artist is of utmost importance. Methodical scientific investigations can help to shed light on these issues.

Multiple timeframes

During the lifetime, an artist typically uses different materials, due to availability and personal choices, and experiment/technical changes. This is more obviously the case for artists of the 20th century, as they could use a large number of materials available in the market, but, it is likely to a lesser extent, that artists from previous centuries also experienced technical evolution over time.

In order to distinguish among various timeframes in an artist's lifetime, his/her materials and technique should be studied during the entire life, to understand the technical choices and evolution. For instance, *Saint Mary Magdalene with a sarcophagus* is attributed to Gianpietrino, a pupil of Leonardo da Vinci; three diverse timeframes were proposed by art historians for this painting: specifically, 1515-20, 1510-20 and 1520-30. The characterisation of the materials showed compatibility with the 16th century and an Italian location, but to classify this object as made by Gianpietrino and at a particular date is a step too far. Therefore, the investigation of other Gianpietrino paintings specified some characteristic features of this artist and in particular of his technical evolution. For instance, based on the imprimatura (both colour and location), flesh tones and a little ability to reach some effects (such as the overlaying of the green layers), the Saint Mary Magdalene painting appears to have been made before 1510, which suggests a new date for this artwork based on scientific evidence, making it a sort of prototype of a series of paintings executed at a later time. In fact, another painting, the *Virgin with child* of the Rijksmuseum, has a confident attribution of about 1510 as the year of execution, and it shows diverse materials and techniques, such as the more dynamic position of the head of the Virgin, that indicate an evolution of the artist.

In this case, scientific analyses and the comparison of the results with the ones of other paintings were an invaluable tool in pinpointing and narrowing down a date for the painting avoiding further dispute over its execution.

Multiple artists

Alternate attributions of the same object to diverse artists instigate disputes among professionals with different views, but also prevent genuine classification of the artwork. To associate the object to a specific artist, the materials characterisation should be compared to the materials and technique of all the artists in question. That means that databases should be available, otherwise only the compatibility with the suggested dating can be carried out.

The study on English portrait miniatures of the 15th – 16th century illustrates this aspect. Some miniatures showed several attributions over time. For instance, P.145-1910 and P.146-1910, portraying two little girls, were traditionally ascribed to artist Levina Teerlinc [1]. A catalogue in 1930 (Catalogue of the Pierpont Morgan collection) expressed doubts over this attribution, and at the moment the two miniatures are attributed to Isaac Oliver[15].

A few studies have produced results for these miniatures over time, but there is still insufficient data for a complete database relating to the artists of that time.

In particular, after an evaluation of 16 miniatures allegedly made by Oliver, the results show that the two little girls seem outliers when compared to Oliver’s technique. Teerlinc’s materials and technique was not deeply investigated [2], therefore the lack of data for comparison did not allow classification of these two objects to a specific artist.

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[15] https://collections.vam.ac.uk/item/O78666/an-unknown-girl-aged-four-portrait-miniature-oliver-isaac/ and http://collections.vam.ac.uk/item/O78667/an-unknown-girl-aged-five-portrait-miniature-oliver-isaac/ (last access 03 July 2019).

5.1 Paysage de montagne

5.1.1 Introduction

The painting (Figure 5.1) was investigated in order to confirm the attribution to the Dutch painter Jan Ruyscher. A previous dendrochronological analysis was carried out and the range 1660-1740 was identified. Even though dendrochronology is a non-invasive technique where the tree rings are counted, in this case it did not gain enough information and the dating range had a degree of uncertainty. Therefore, a further investigation of the object with several techniques was required, with the aim of proposing a more certain date, which would have helped the authenticity. For this reason, radiocarbon dating and spectroscopic techniques were combined together in a multi-analytical methodology. Part of the research was carried out in the Ion Beam Laboratory, ETH Zurich.

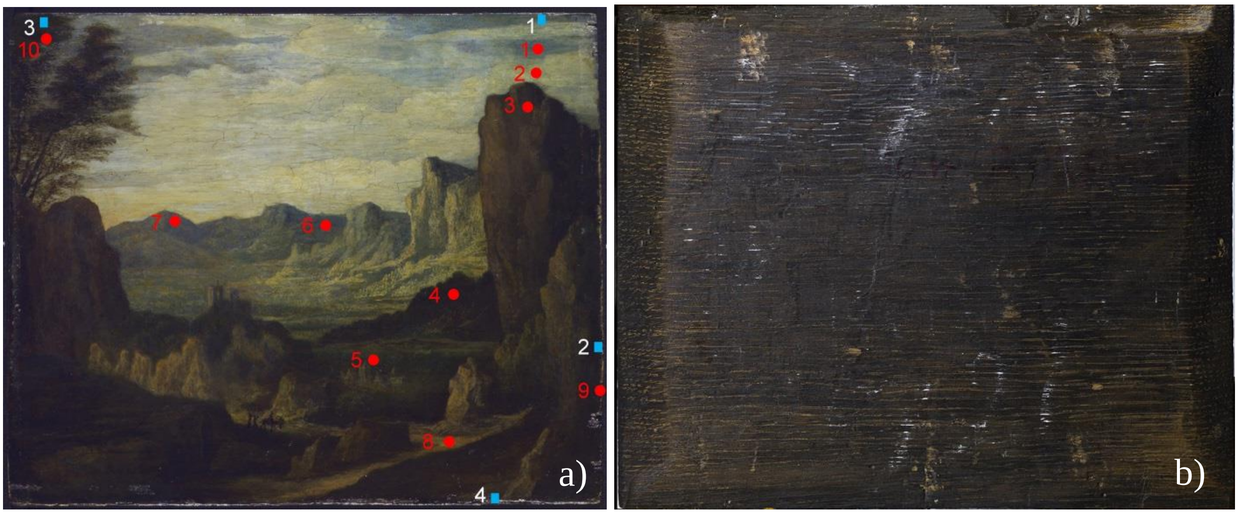

Figure 5.1. *Paysage de montagne*, Jan Ruyscher (attributed), 17th century, oil on panel, private collection. a) Visible light photography of the painting, the measured spots by XRF are indicated as red circles, while the sampled areas for further analysis as cross-sections are designated by the blue squares; b) reverse of the painting.

5.1.2 Results of non-invasive analyses

The materials characterisation started with non-invasive analyses (multispectral imaging, XRF).

Preliminary documentation by means of multispectral imaging (Figure 5.2) assessed an overall good state of conservation of the painting, which shows a flat surface without colour losses. However, UV fluorescence highlighted the presence of a thick final varnish covering almost the whole surface; several restored areas are present and a peculiar bright yellow fluorescence colour on the trees at the left side is observed. On the back of the panel, a writing, especially visible under UV, links the object to Jan Ruyscher.

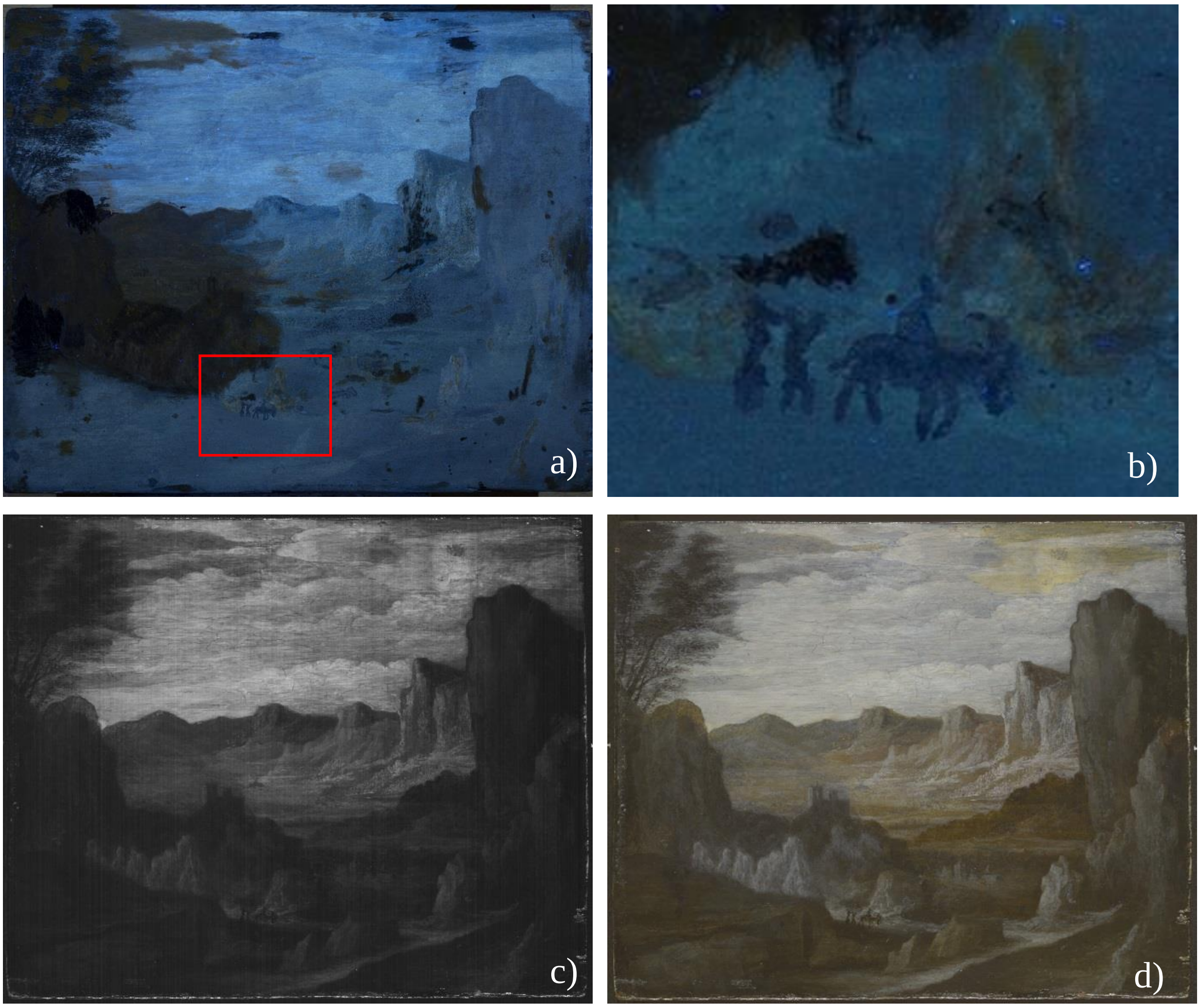

Figure 5.2. a) UV fluorescence photography and b) magnification of the area indicated within the red square, c) Infrared reflectography (900 nm), d) Infrared reflectography False Colour.

The elemental composition of the main pigments used in the painting under study was investigated by XRF (Figure 5.1 and Table 5.1). In all examined location, the identification of titanium, barium and zinc all over the painting indicates a general use of titanium white, barium sulfate, zinc oxide (zinc white) or zinc sulfide (which associated to barium sulfate is characteristic of lithopone). These pigments were introduced in the art market starting from the 18th century, therefore further investigation in cross-section was necessary to assess whether these pigments were used in the original layers or belonged to restoration materials. Calcium, which may be present in the form of carbonate or sulfate, iron, probably ochres or green earth (on green spots 4 and 5 in Figure 5.1) and/or earth pigments when manganese is also identified, and small amounts of lead, likely linked to lead white, were found to be omnipresent. In the blue sky as well as the restored blue mountain (location marked as 1 and 7) some cobalt was also found, which hints to the use of cobalt blue. The non-restored area of the blue mountain (spot 6) however does not show any cobalt, or any other element characteristic for blue.

Table 5.1 Elements identified by XRF analysis, correlated to their location and with a possible interpretation.

Spot	**Location**	**Elements identified**	**Possible pigments interpretation**
1	Blue sky	Ca, **Ti/Ba**, (Mn), Fe, Co, **Zn**, Pb	Titanium white, barium sulfate, zinc white, earth pigments, cobalt blue, calcium carbonate, lead white, ultramarine blue(?)
2	White sky	Ca, **Ti/Ba**, (Mn), Fe, **Zn**, (Pb)	Zinc white, titanium white, barium sulfate, calcium carbonate, earth pigments, lead white
3	Brown mountain	Ca, **Ti/Ba**, Mn, **Fe**, **Zn**, Pb	Titanium white, barium sulfate, zinc white, earth pigments, calcium carbonate, lead white
4	Dark green forest	Ca, **Ti/Ba**, Mn, **Fe**, **Zn**, Pb	Titanium white, barium sulfate, zinc white, earth pigments, calcium carbonate, lead white
5	Green land	Ca, **Ti/Ba**, (Mn), **Fe**, **Zn**, Pb	Zinc white, earth pigments/ green earth, titanium white, barium sulfate, lead white, calcium carbonate
6	Blue mountain	Ca, **Ti/Ba**, Fe, **Zn**, Pb	Zinc white, titanium white, barium sulfate, lead white, calcium carbonate, ochres, ultramarine blue(?)
7	Blue mountain (restored area)	Ca, **Ti/Ba**, Fe, Co, **Zn**, **Pb**	Zinc white, titanium white, barium sulfate, lead white, ochres, calcium carbonate, cobalt blue
8	Light brown path	Ca, **Ti/Ba**, (Mn), **Fe**, **Zn**, Pb	Zinc white, titanium white, barium sulfate, earth pigments, calcium carbonate, lead white
9	White ground	Ca, **Ti/Ba**, (Mn), **Fe**, **Zn**, Pb	Zinc white, titanium white, barium sulfate, earth pigments, calcium carbonate, lead white
10	Green trees	Ca, **Ti/Ba**, (Mn), Fe, **Zn**, Pb	Titanium white, barium sulfate, zinc white, earth pigments, calcium carbonate, lead white

5.1.3 Conclusion on the Paysage de montagne

The non-invasive analyses carried out on the painting have revealed a few features that raise doubts about the authenticity of this object.

XRF spots on original areas underlined the presence of elements – titanium, barium and zinc – that can be allegedly associated to pigments used after the 18th century. Titanium is likely present as titanium white, commercialised since 1919 [3], but at this stage it is not possible to distinguish between anatase and rutile form. Barium is possibly related to barium sulfate, used as a pigment since late 18th century [4]. The use of zinc oxide as pigment began in the late 18th century [5], while in its sulphide form and in combination with barium sulfate, commonly known as lithopone, was commercialised in 1874 [5].

The attribution to the painter Ruyscher, who lived in the 17th century, is then disproved and the artwork becomes an unknown painting; further analyses on cross-sections will help in the characterisation of the materials (both organic and inorganic) and a classification of the object will be proposed (see section 6.2).

5.2 Mon Amour

5.2.1 Introduction

The painting *Mon Amour* of private collection was investigated in order to corroborate or disprove the attribution to Pablo Picasso. The presence of a signature and a previous stylistic evaluation corroborated the attribution, but scientific analyses were required to further investigate the object[16].

Mon Amour shows a very common subject among Picasso's paintings (Figure 5.3): between 1911 and 1916, the artist produced a conspicuous series of still life with musical instruments [6, 7]. The painting, which has Picasso's signature on the top left side, was hypothesised to be depicted around 1915[17] by means of stylistic evaluation.

The first step of the methodology consisted in the examination of materials in order to define a chronological range, likely fitting with Picasso's lifetime. As a stylistic study disclosed a possible period of time for the execution of the painting (around 1915), the materials' information can be narrowed down to that timeframe, testing the compatibility. Moreover, to find evidence for the attribution to Picasso, then objectively linking an artwork to an artist, technical data about his paintings were systematically collected based on published literature, and the results compared with the ones obtained from the object being studied.

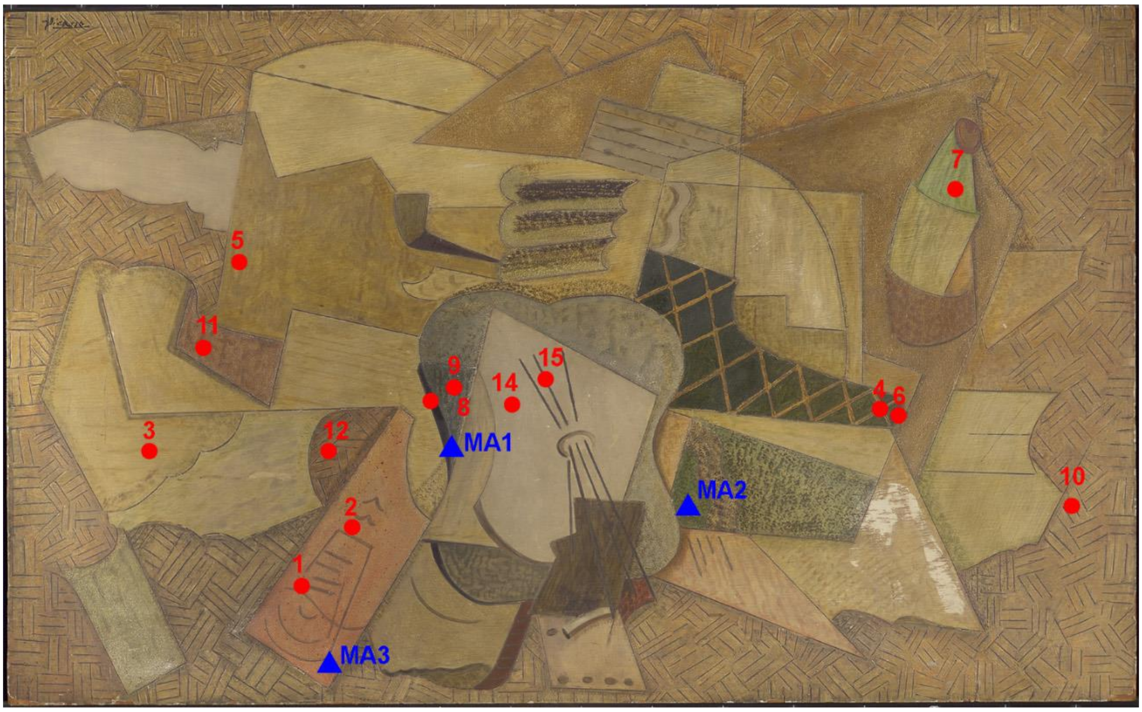

Figure 5.3. *Mon Amour*, P. Picasso (attributed), 160x99 cm, tempera on cardboard, private collection. The red circles indicate the XRF analyses spots, the blue triangles are related to the sampled areas for the cross-sections investigations.

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[16] Part of this paragraph is published in Fiorillo F. *et al.*, *A multi-analytical approach for the characterisation of 20th century paintings*, 2019, Eur. Phys. J. Plus, 134: 373. DOI: 10.1140/epjp/i2019-12752-5.

[17] Expertise by Prof. U. Gentile, 1978.

5.2.2 Materials and methods

The painting was examined by means of non-invasive analyses (multispectral imaging, XRF), then three samples were collected in order to characterise different colours: blue (MA1), green (MA2), red (MA3). The cross-sections were analysed with SEM-EDS, FTIR and Raman microscopy.

5.2.3 Results: materials characterisation

In this specific case, imaging techniques performed as first step of the methodology did not show any particular feature concerning the painting (data not shown here[18]).

The possible pigment interpretation by means of XRF (Table 5.2) was not thoroughly informative, since the same elements were detected in all spots. Exception is represented by Cr, found only in two green areas. Yellow and black/brown areas were not taken into consideration because, although the presence of organic materials was possible, the first probably contained ochres, as the presence of a higher level of iron in comparison to the red areas suggested, and the latter were likely made of bone black due to the presence of phosphorus. Light blue areas did not show any element associated to a blue pigment: ultramarine blue and/or organic blue pigments, non-detectable by XRF, could be present and therefore a sample was collected. Moreover, green areas could be obtained with green pigments or mixtures of blue and yellow ones: a second sample was taken to understand this technical choice. Finally, a red sample was collected in order to investigate the presence of organic colourants. Cross-sections were investigated layer by layer and the results are shown in Table 5.3.

Table 5.2. XRF results and interpretation. The recognised elements are indicated along with their possible interpretation.

N.	Area	Elements identified	Possible pigment interpretation
1	Red	P, Ca, Ba, Mn, Fe, Zn, Pb	Calcium carbonate and/or calcium sulfate, barium sulfate, zinc white and/or zinc sulfide (lithopone?), lead white, bone black, earth and umber pigments
2	Orange	P, Ca, Ba, Mn, Fe, Zn, Pb	Calcium carbonate and/or calcium sulfate, lead white, barium sulfate, zinc white and/or zinc sulfide (lithopone?), earth and umber pigments, bone black
3	Light yellow	Ca, Ba, Mn, Fe, Zn, Pb	Lead white and/or lead oxides, barium sulfate, zinc white and/or zinc sulfide (lithopone?), earth and umber pigments, calcium carbonate and/or calcium sulfate
4	Yellow	Ca, Ba, Mn, Fe, Zn, Pb	Earth and umber pigments, barium sulfate, lead white, zinc white and/or zinc sulfide (lithopone?), calcium carbonate and/or calcium sulfate
5	Dark yellow	P, Ca, Ba, Mn, Fe, Zn, Pb	Lead white and/or lead oxides, calcium carbonate and/or calcium sulfate, barium sulfate, zinc white and/or zinc sulfide (lithopone?), earth and umber pigments
6	Dark green	P, Ca, Ba, Cr, Mn, Fe, Zn, Pb	Calcium carbonate and/or calcium sulfate, bone black, barium sulfate, earth and umber pigments and Prussian blue(?), zinc white and/or zinc sulfide (lithopone?), lead white, chrome green and/or chrome yellow

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[18] Étude multispectrale “Mon Amour, Nature morte sur Guéridon”, 2013, by LTMI Lumiere Technology Multispectral Institute, Geneve – Paris [31].

7	Light green	Ca, Ba, Cr, Fe, Zn, Pb	Lead white, barium sulfate, zinc white and/or zinc sulfide (lithopone?), Fe oxides and/or Prussian blue, calcium carbonate and/or calcium sulfate, chrome green and/or chrome yellow
8	Dark blue	P, Ca, Ba, Mn, Fe, Zn, Pb	Prussian blue, earth and umber pigments, bone black, calcium carbonate and/or calcium sulfate, lead white, zinc white and/or zinc sulfide (lithopone?), barium sulfate
9	Light blue	P, Ca, Ba, Mn, Fe, Zn, Pb	Lead white, calcium carbonate and/or calcium sulfate, earth and umber pigments, Prussian blue(?), bone black, zinc white and/or zinc sulfide (lithopone?), barium sulfate
10	Light brown	P, Ca, Ba, Mn, Fe, Zn, Pb	Lead white, calcium carbonate and/or calcium sulfate, bone black, earth and umber pigments, zinc white and/or zinc sulfide (lithopone?), barium sulfate
11	Brown	P, Ca, Ba, Mn, Fe, Zn, Pb	Bone black, calcium carbonate and/or calcium sulfate, lead white, earth and umber pigments, zinc white and/or zinc sulfide (lithopone?), barium sulfate
12	Brown	P, Ca, Ba, Mn, Fe, Zn, Pb	Bone black, calcium carbonate and/or calcium sulfate, lead white, earth and umber pigments, zinc white and/or zinc sulfide (lithopone?), barium sulfate
13	Grey	Ca, Ba, Mn, Fe, Zn, Pb	Lead white, zinc white and/or zinc sulfide (lithopone?), barium sulfate, earth and umber pigments, calcium carbonate and/or calcium sulfate
14	Black	P, Ca, Ba, Mn, Fe, Zn, Pb	Lead white, bone black, zinc white and/or zinc sulfide (lithopone?), barium sulfate, earth and umber pigments, calcium carbonate and/or calcium sulfate

Ground layer. A single layer of white preparation was laid directly on top of the support. Calcium and sulfur in SEM–EDS spectra were possibly linked to calcium sulfate; a few particles made of strontium and sulfur were recognised as well, likely associated to celestine ($SrSO_4$), an impurity of gypsum [8]. Si, Al, Mg and Na were possibly related to the presence of silicates. FTIR and Raman microscopies identified di-hydrated calcium sulfate. Additionally, Raman spectrum shows also the anhydrous form (Figure 5.4) [9].

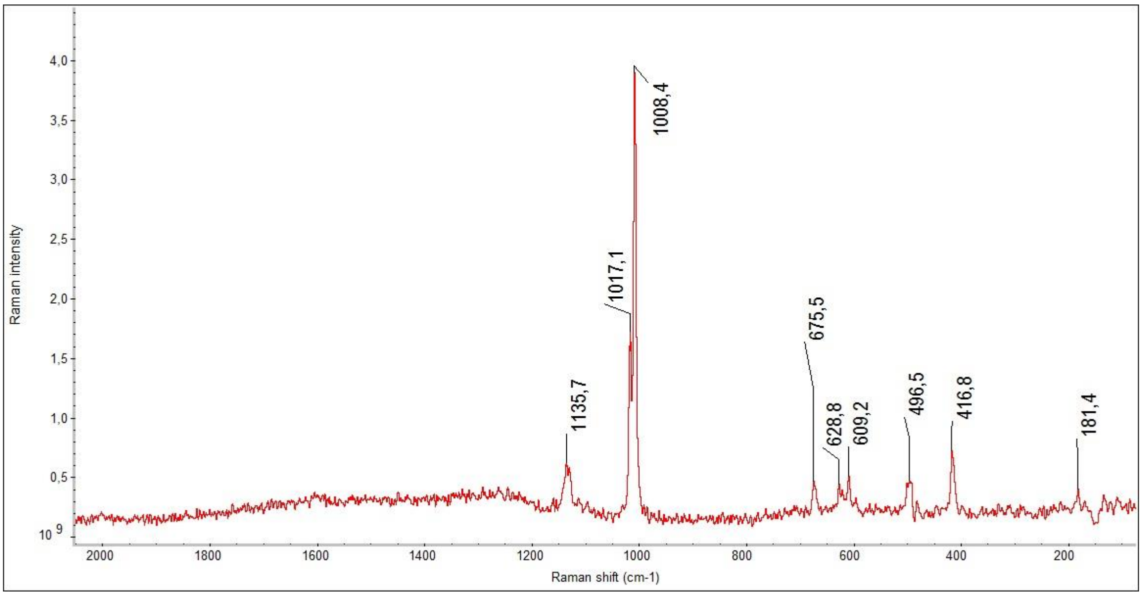


Figure 5.4. Raman spectrum collected on the ground layer of *Mon Amour*, showing bands related to di-hydrated (496, 1008, 1136 cm^{-1}) and anhydrous (417, 496, 609, 629, 676, 1017 cm^{-1}) calcium sulfate.

Pictorial layers. The light blue sample collected on the guitar (MA1) consisted of a single pictorial layer. The main element in the SEM-EDS spectra was lead, likely to be associated to lead white, and small amounts of zinc were also found. A few white particles are made of barium and sulfur, likely linked to barium sulfate, and the blue ones contain sodium, aluminium, silicon and potassium, likely to be ultramarine blue [5]. Few red grains are made of iron and manganese and possibly identified as earth and umber pigments. The presence of calcium and phosphorus in the black particles suggested the presence of bone black. FTIR confirmed lead white and di-hydrated calcium sulfate, while FTIR bands at 1657 and 1544 cm^{-1} could be related to a protein, while the one at 1726 cm^{-1} was associated to a lipid substance. Thus, the binder could be an egg tempera or a mixture of animal glue and oil. Raman microscopy confirmed ultramarine blue; the round shape of the particles under the microscope allowed to hypothesise an artificial nature of this pigment [5].

The SEM-EDS spectra on the green sample (MA2) identified lead as the main element, likely linked to lead white. A few coarse green particles are made of barium and sulfur, possibly associated to barium sulfate; a few red particles consisted of iron and manganese, likely related to earth and umber pigments (with zinc impurities), very few black grains contained calcium and phosphorus, possibly linked to bone black, and the tiny yellow ones were made of chromium and lead, possibly as chrome yellow (Figure 5.5). FTIR confirmed the presence of lead white and also identified di-hydrated calcium sulfate, calcium carbonate and Prussian blue (Figure 5.6).

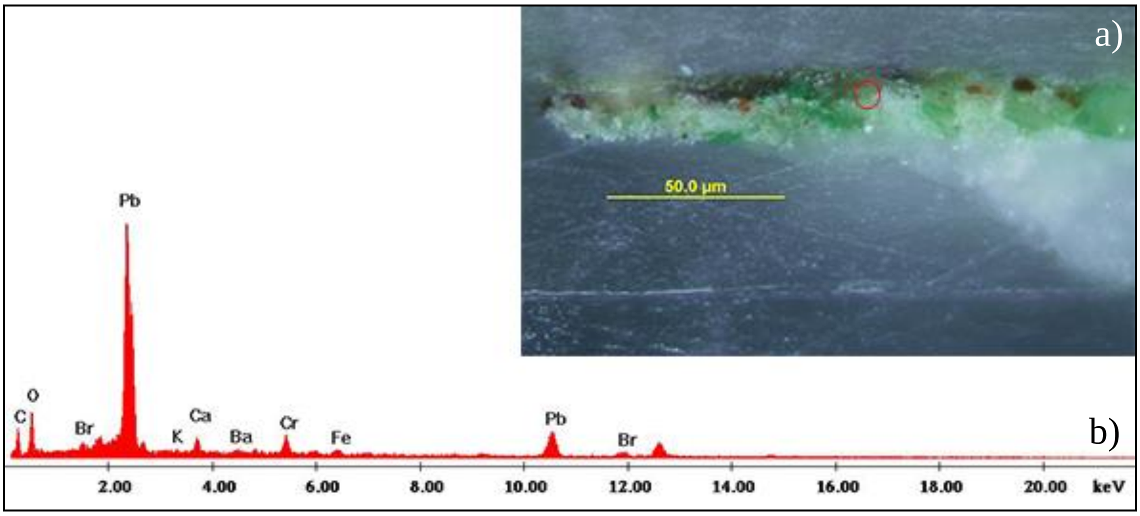


Figure 5.5. a) Cross section of MA2, the red circle indicates the yellow particle investigated; b) SEM-EDS spectrum obtained from the yellow particle, chromium could be associated to chrome yellow.

The presence of organic materials was identified by the bands at 2928, 2848, 1730, associated to an ester, and 1661 (amide I) and 1541 cm^{-1} (amide II), which identified a protein. Barium sulfate and Prussian blue were confirmed by Raman microscopy, while the sporadic yellow particles failed to produce a Raman spectrum. Therefore, the green was obtained with a mixture of a blue and a yellow pigment, while the presence of white pigments helped to achieve a lighter characteristic hue.

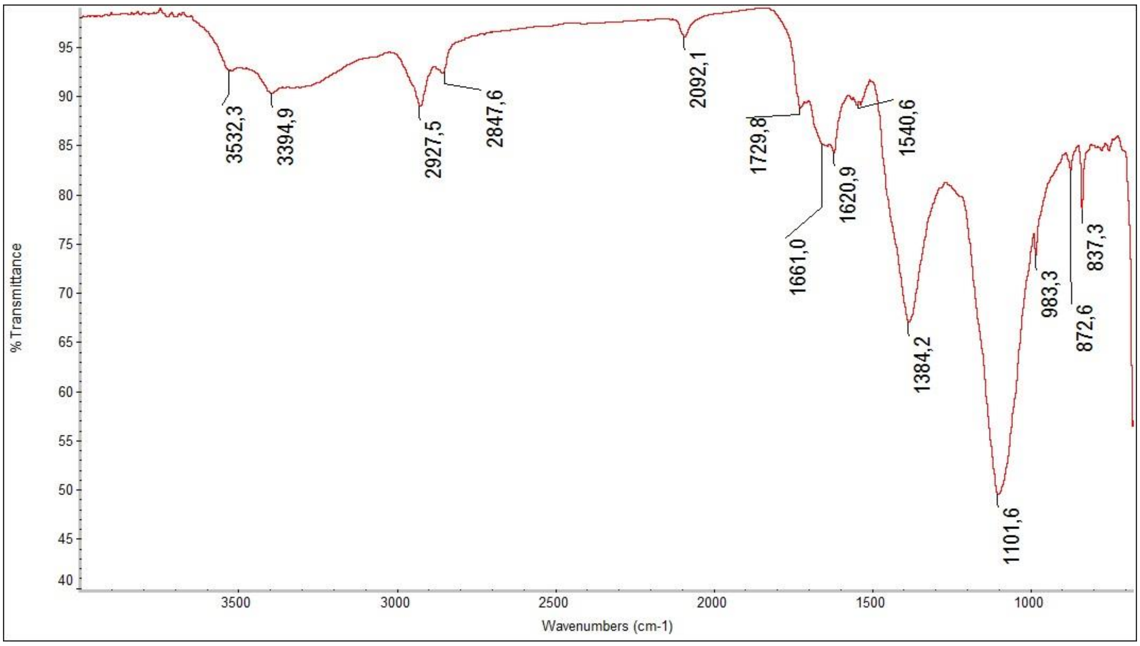


Figure 5.6. FTIR spectrum of the green layer of MA2. The compounds identified are di-hydrated calcium sulphate (3532, 3395, 1621, 1102, cm^{-1}), organic materials (2928, 2848, 1730, 1661, 1541 cm^{-1}), Prussian blue (2092 cm^{-1}), calcium carbonate (1384, 873 cm^{-1}) and lead white (1384, 837 cm^{-1}).

The SEM-EDS analyses on the red sample (MA3) showed lead as the predominant element, likely linked to lead white, and small amounts of calcium. Some particles contained calcium and sulfur and others barium and sulfur, possibly related to calcium sulfate and barium sulfate, respectively. By means of micro-Raman, a red synthetic organic pigment was identified as PR3 (*Colour Index Generic Name* Pigment Red 3, *Colour Index Number* 12120, Toluidine Red) (Figure 5.7) [10].

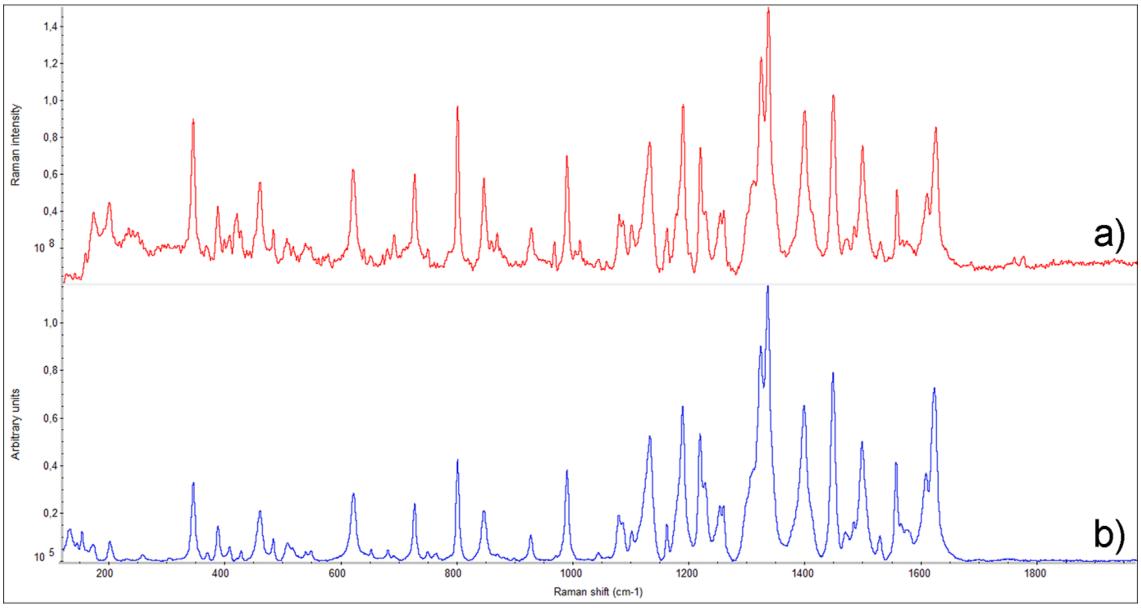
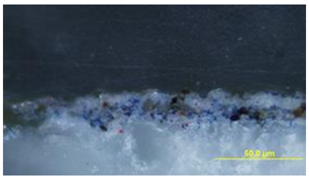
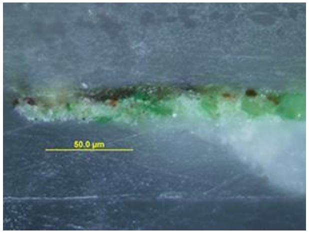
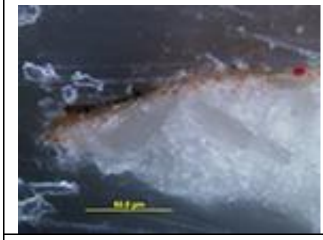


Figure 5.7. Comparison between Raman spectra of a) the red layer of MA3 and b) PR3 reference [10].

In conclusion, based on the organic and inorganic materials identified in *Mon Amour*, a timeframe of painting creation could be established. Some pigments were indeed used since ancient times (earth pigments, bone black, lead white), Prussian blue since the beginning of 18th century, other compounds from 19th century, such as barium sulfate and synthetic ultramarine [5]. PR3 was first synthesised in 1905 [11], providing a *post quem* date spanning up to nowadays.

Table 5.3. Summary of the analyses carried out on the three cross-sections of *Mon Amour*, combining the results of FTIR, SEM-EDS and Raman microscopy for both the pictorial layers and ground.

Cross-section, number and colour	**SEM-EDS**	**FTIR (cm^{-1})**	**Raman (cm^{-1})**	**Pigment interpretation**
MA1, Blue 	Na, Mg, Al, Si, P, Pb, S, Ca, Ba, Mn, Fe, Zn	1726, 1657, 1544 (organic material) 3529, 3394, 1110 (di-hydrated calcium sulphate) 1382, 838 (lead white)	1053 (lead white) 547 (ultramarine blue)	Lead white ($2PbCO3\cdot Pb(OH)_2$) ultramarine blue ($Al_6Na_8O_{24}S_3Si_6$) barium sulphate ($BaSO_4$) bone black (Ca phosphate) earth pigments (Fe, Mn oxides, clay) di-hydrated calcium sulphate binder: protein, lipid
MA2, Green 	Fe, Mn, Zn, Ca, P, Cr, Pb	2928, 2853, 1729, 1661, 1539 (organic material) 1384, 873, 837 (calcium carbonate, lead white) 1102, 1621, 3533, 3395 (di-hydrated calcium sulphate) 2092 (Prussian blue)	988 (barium sulphate), 2156, 2120, 2094 605, 536, 459, 280 (Prussian blue)	Prussian blue (Fe(III) hexa-cyanoferrate(II) Pb chromates lead white ($2PbCO3\cdot Pb(OH)_2$) barium sulphate ($BaSO_4$) di-hydrated calcium sulphate bone black (Ca phosphate) earth pigments (Fe, Mn oxides, clay) binder: protein, lipid
MA3, Red 	Mg, Al, Si, Pb, S, Ca, Ba	-	PR3	Lead white ($2PbCO3\cdot Pb(OH)_2$) Red synthetic pigment PR3, barium sulphate ($BaSO_4$) calcium sulphate silicates
White ground	Na, Mg, Al, Si, Sr, S, Ca	3529, 3397, 1683, 1619, 1106 (di-hydrated calcium sulphate)	1135, 1008, 674, 494, 417 (di-hydrated calcium sulphate) 1160, 1017, 626, 609 (anhydrous calcium sulphate)	Di-hydrated and anhydrous calcium sulphate strontium sulphate ($SrSO_4$) silicates

5.2.4 Comparison with other works by the same artists

Based on a literature overview of Picasso's technical studies, a comparison of the findings with reference information provided compatibility with the artists' technique. A summary of previous published technical results for pigments characterisation is reported in Table 5.4 and Table 5.5.

Even though Picasso created a great amount of paintings during his long lifetime, only a few high-quality studies are published. As regards *Mon Amour*, results of the scientific tests here performed identified the range 1905-present time as period of creation. A prior presumed date through a purely stylistic evaluation indicated the first half of the 1910s, corroborating the analytical findings and narrowing the timeframe. Though, there is a lack of scientific papers about Picasso's artworks in that period, further comparisons could be made based on the identified pigments.

Zinc white was used as main white at least until 1946, sometimes mixed with barium white, titanium white or lithopone [12, 13]. In other cases, lead white [14–18] or titanium white [12, 19] was utilised – in this view, it seems worthwhile noticing that the identification of rutile in the *Guitar* painting [19] does not fit the timeframe of synthetic cubism (1912-14), as this form of titanium white was widely used only after 1945 [3], therefore the already uncertain attribution of this artwork to Picasso may be reconsidered.

The blue was mostly Prussian blue, cobalt blue and ultramarine blue [12, 13, 15–17], while the red pigments could be vermilion and ochres [13–16], red lead [12, 15], cadmium red [17] or synthetic pigments as PO34 [19].

Finally, the main green pigments were emerald green [13, 14, 16] and chromium compounds [14–16], but it was found that a mixture to obtain the green could also be applied, for instance chrome yellow and Prussian blue [16] or cadmium yellow and ultramarine blue [17].

In this case all the materials identified in *Mon Amour* are compatible with the ones found in published literature, with the novelty of the presence of PR3.

5.2.5 Conclusion on the *Mon Amour*

First of all, the methodological approach used in this research enabled the characterisation of materials and techniques of 20th century paintings. Such an approach led to the identification of complex mixtures of both organic and inorganic compounds.

All the pigments and binders identified were chronologically compatible with the art history of 20th century; *Mon Amour* could have been painted since 1905 because of the presence of PR3 commercialised in that year, thus it is also compatible with the period around 1915, as identified by a stylistic study as a possible timeframe for the execution of the artwork.

A comparison with previous published data showed that the artwork is compatible with Picasso's materials, only the presence of PR3 was recognised as novelty.

Regardless this positive evidence, it should be clear that ascertainment of authentication of paintings cannot be provided because other information needs to be taken into consideration, such as further scientific analyses, art-historical and provenance studies on other artworks.

The painting under study can be an original one, but also a copy made in the manner of Picasso; eventually an examination of the signature can also hint at a possible fraudulent aim, if found not compatible with Picasso's writing. The attribution to Picasso, although corroborated by a stylistic evaluation, in this case cannot be confirmed because no information is available about his materials and technique around approximately 1915.

Table 5.4. Published data on paintings attributed to Picasso. For each painting the identified pigments are expressed (a question mark indicates a suggested pigment).

		Man in a beret - 1895	Portrait of an old man – 1895	Self-portrait with a wig – 1898/1900	Portrait of Carles Casagemas – 1899	Portrait of a man in the style of El Greco – 1899/1900	Portrait of Josep cardona I Furrò – 1899/1900	The blue room - 1901	Violon Ceret - 1912	Still life - 1914	Harlwquin Musician - 1924	Harlequin - 1927	Nude woman in a red armchair - 1932	The Dreamer - 1932	Reading at a table - 1934	Woman asleep at a table - 1936	Weeping woman - 1937	Femme au chapeau assis sur une chaise -1938	17 artworks in Antibes - 1946	Guitar*
White	Lead white	✓		✓	✓	✓[b]	✓	✓	✓		✓	✓		✓	✓	✓			✓	
	Zinc white	✓				✓	✓	✓			✓	✓		✓		✓		✓	✓	
	Barium sulfate			✓	✓	✓	✓	✓			✓			✓		✓		✓	✓	
	Lithopone										✓								✓	
	Ti white (an.)															✓			✓	✓
	Ti white (rut.)																			✓
	$CaCO_3$	✓		✓		✓	✓					✓				✓		✓	✓	✓
	Gypsum							✓			✓	✓		✓	✓			✓a)	✓	
	Kaolin	✓		✓																
Blue	Prussian blue	✓	✓	✓	✓	✓	✓	✓			✓							✓	✓	
	Cobalt blue	✓		✓			✓				✓									
	Ultramarine blue	?					?	✓			✓			✓						
	PB15																			✓
Red	Red ochre		?	✓		?	✓		✓		✓					✓		✓	✓	
	Umber/ earth	✓	✓	✓	✓	✓	✓				✓	✓				✓		✓	✓	
	Red lead			?	?	?													✓	
	Vermilion			✓	✓	✓	✓	✓			✓				✓			✓		
	Cd red													✓						
	Organic red										✓									✓e)
Green	Emerald green					?		✓						✓				✓		
	Chrome green			?	?	?		✓						✓						
	PG7																			✓
	Organic green																		✓	
Yellow	Cr yellow			✓	?c)	?		✓			✓[d]							✓	✓	
	Cd yellow							✓			✓							✓		
	Yellow ochre	✓		✓	✓	✓					✓								✓	

	Co violet	?																✓		
Black	C-based black			?	✓	?	?	✓			✓	✓			✓	✓		✓	✓	
	Fe-based black			?	✓	?	?												✓	
	Asphalt								?										✓	
	Ivory/bone black	✓	✓	✓	✓	✓	✓	✓			✓									
	Mn oxides		✓	✓		✓														
BINDERS	Oil	✓	✓	✓	✓	✓	✓		✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓
	Natural wax											✓		✓	✓					✓
	Animal fats									?										
	Ripolin																	✓		
	Natural resin											✓			✓	✓			✓	✓
	Alkyd resin												?							

[a] Hemi-hydrate calcium sulfate; b) lead sulfate; c) or strontium yellow; d) orange lead chromate; e) PO34.

Table 5.5. Techniques used for the study of the paintings found in published literature.

			Man in a beret - 1895	Portrait of an old man – 1895	Self-portrait with a wig – 1898/1900	Portrait of Carles Casagemas – 1899	Portrait of a man in the style of El Greco – 1899/1900	Portrait of Josep cardona I Furrò – 1899/1900	The blue room - 1901	Violon Ceret - 1912	Still life - 1914	Harlequin Musician - 1924	Harlequin - 1927	Nude woman in a red armchair - 1932	The Dreamer - 1932	Reading at a table - 1934	Woman asleep at a table - 1936	Weeping woman - 1937	Femme au chapeau assis sur une chaise - 1938	17 artworks in Antibes - 1946	Guitar*
NON-INVASIVE	Multispectral Imaging	UV								✓			✓		✓	✓	✓				✓
		IR R	✓	✓	✓	✓	✓	✓	✓	✓			✓		✓	✓	✓				
		X Rad.	✓	✓	✓	✓	✓	✓					✓		✓	✓	✓				
	Luminescence imaging								✓[b]			✓[b]									
	Superficial analysis	PLM										✓							✓	✓	
		UV-Vis	✓	✓	✓	✓	✓	✓		✓		✓								✓[e]	
		FORS								✓		✓									
		XRF	✓	✓	✓	✓	✓	✓	✓[c]	✓		✓	✓		✓	✓	✓		✓	✓	
		FTIR	✓[a]	✓[a]	✓[a]	✓[a]	✓[a]	✓[a]		✓										✓	
		Raman	✓	✓	✓	✓	✓	✓													
MICRO-DESTRUCTIVE	Cross-sections or samples	SEM-EDS							✓	✓		✓	✓		✓	✓	✓			✓	✓
		FTIR							✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
		Raman							✓				✓		✓	✓	✓		✓	✓	✓
		Py-GC-MS								✓	✓[d]		✓	✓	✓	✓	✓	✓			✓

a) FTIR in the NIR and MIR range;, b) and also reflectance imaging spectroscopy, c) also synchrotron radiation x-ray fluorescence (SR-XRF), d) Thermally-assisted hydrolysis and methylation (THM); e) UV/vis-NIR FORS, UV-Vis Fluo

5.3 Angel holding a *tabula ansata*

5.3.1 Introduction

Having previously established that the inscription on the back of the painting ("A. D. 1764 A. R. M. fc. Roma") is not entirely accurate, as Mengs never visited Foligno when he was in Italy, the aim of this investigation was the evaluation of 1764 as year of execution. In this view, new insights could be gathered about the nature of the object.

5.3.2 Materials characterisation

Scientific investigations allowed to deepen the study of the materials used by the artist. Three samples were collected from the painted surface in order to obtain cross-sections and analyse them with several techniques (see Appendix A.03). A white ground layer is found for all the samples and consists mostly of Pb, likely linked to lead white. This kind of preparation is characteristic of artworks painted from the half of 18th century [20].

The analyses of the pictorial layers of a sample collected on a yellow area (Figure 5.8) show the presence of zinc, possibly associated to zinc white (Figure 5.9). This pigment is used since the end of the 18th century and widely commercialised since 1834 [5]. Yellow particles are characterised by the presence of lead and antimony, which may indicate the use of Naples yellow (Figure 5.9). By means of Raman, the band at 125 cm^{-1} could be related to lead antimonate (Naples yellow) [21, 22], along with bands at 518 and around 300 cm^{-1} (Figure 5.10, spectrum a). The dominant band around 120-140 is attributed to Pb-O stretching mode, but several studies have found a shifting in its position, due for instance to the firing temperature when mixing the oxides [21] or to the Pb:Sb ratio [23], therefore it is not a diagnostic peak for the characterisation of the compound. Bands at 518 and around 300 cm^{-1}, on the other hand, are characteristic of Naples yellow.

The band at 976 cm^{-1} is associated to lead sulfates [23]. The spectrum collected on white grains corresponds to lead white (Figure 5.10, spectrum b): the characteristic band is at 1050 cm^{-1}, and a second one is around 110 cm^{-1}. Spectrum c collected on a white grain corresponds to the mineral rosiaite ($PbSb_2O_6$), with the typical bands at 658 and 120 cm^{-1} [24, 25].

Lead antimonate was highly popular in Europe between approximately 1750 and 1850, and then was gradually replaced by other pigments [26].

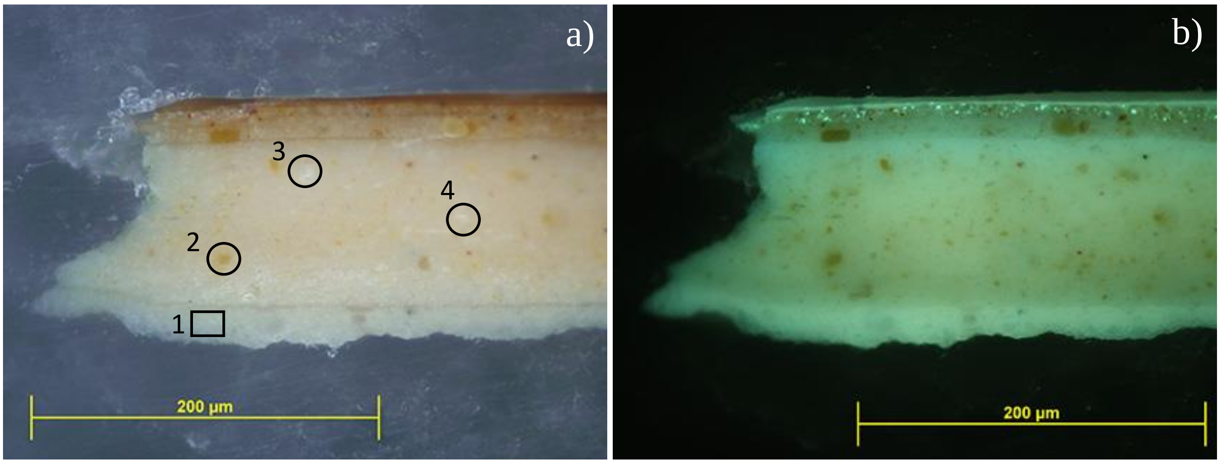


Figure 5.8. a) Cross-section of the yellow sample, b) UV. Areas of analyses are indicated in a).

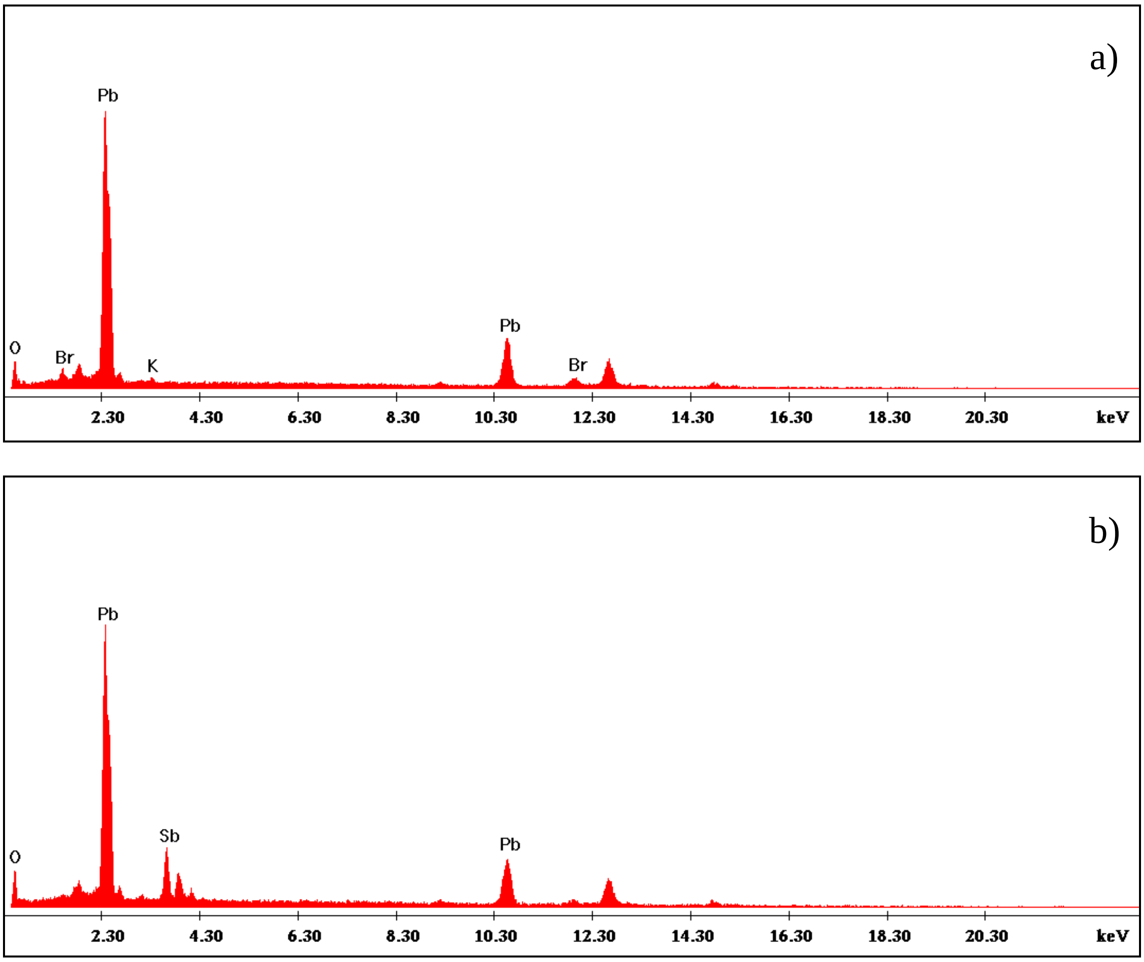


Figure 5.9. a) SEM-EDS spectrum from an area (nr. 1 in Figure 5.8) on the ground layer, the presence of Pb is likely associated to lead white; b) SEM-EDS spectrum on a yellow grain (nr. 2) of the yellow layer.

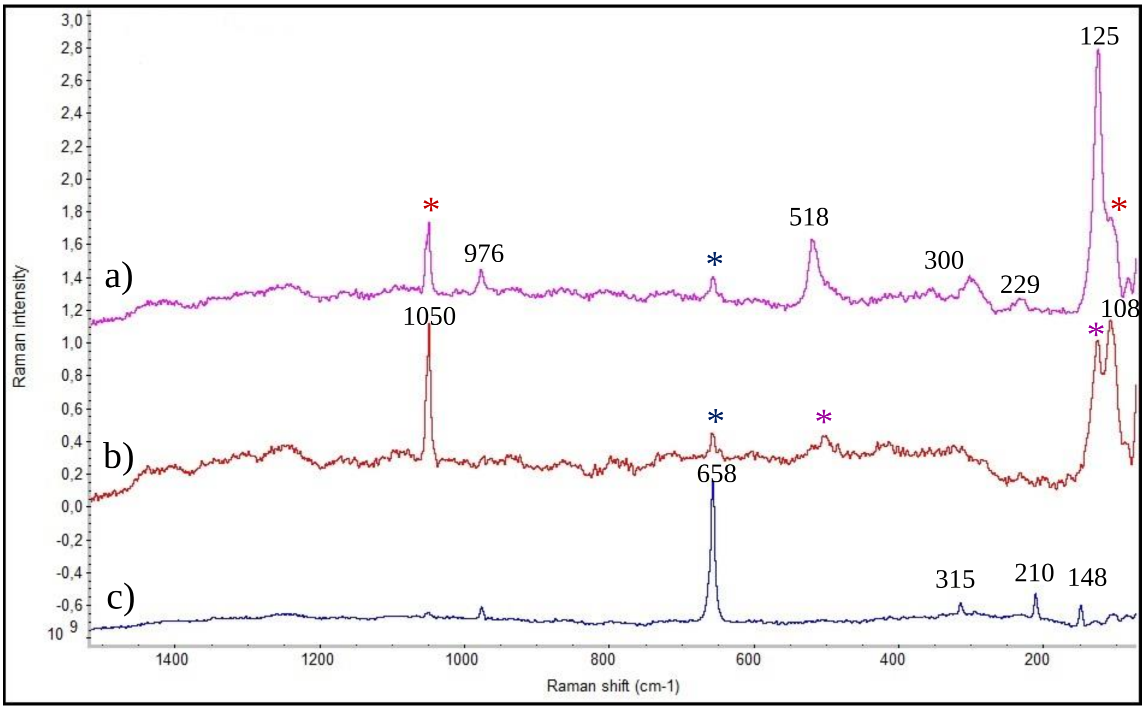


Figure 5.10. Raman spectra collected on the yellow layers, corresponding to particles a) nr.2, b) nr.3 and d) nr.4 in Figure 5.8.

5.3.3 Conclusion on the *Angel*

The information readable on the back of the painting, suggesting a year, a location and an artist, are checked with the help of scientific analyses in order to understand the type of object.

The investigation of the cross-sections allowed to detect Pb, and likely lead white, in the ground layer, which is typical starting from the half of the 18th century. The identification of zinc as likely zinc white, in use since 1782, and lead antimonate, used until approximately 1850, suggested the time range 1782-1850 for the painting execution. Therefore the year indicated on the back, 1764, is not compatible with the painting's materials.

The hypothesis suggested here is that the artwork is a study-copy — perhaps a foreigner student engaged in the *Grand Tour* during the 19th century — as the reproduction of Raffaello's model is quite accurate but less refined in drawing and technique.

However, the inscription on the back suggests a fraudulent aim, attempting to sell the *Angel with tabula ansata* as Mengs artwork: the year is congruous with Mengs chronology but the place (Rome) betrays the intention of who wrote the inscription but did not know the German artist's biography. However, it is not clear if the author of the painting wrote the inscription or if it was added later by a merchant. The inscription revealed a fraud aim but it is not possible to assume the same for the artwork's creation. Finally, the artwork can be classified as a counterfeited study-copy.

5.4 The columbine

5.4.1 Introduction

The painting *The Columbine* was sold by Christie's in 2012 as "Follower of Leonardo da Vinci, 16th century". In order to evaluate the chronological attribution several aspects were investigated.

The painting (68 x 50.3 cm) (Figure 5.11) is possibly a copy or a replica of the one displayed at the State Hermitage Museum of Saint Petersburg and painted by Francesco Melzi, one of Leonardo da Vinci's pupil. Numerous copies of the Melzi's paintings are also certified.

Figure 5.11. *Columbine*, Follower of Leonardo da Vinci, 16th century, oil on panel, private collection.

5.4.2 Art historical research

An art historical research has been carried out. The model of the Columbine was included as one of the portraits created by Leonardo. Several copies were painted during the time, especially between 17th and 18th centuries, and one of them is the painting on display at the State Hermitage Museum, that after several different attributions seems now to be unanimously attributed to Melzi [27].

5.4.3 Materials and methods

The first step of the methodology consists in the documentation by multispectral imaging (UV photography, raking light photography, IR reflectography) and XRF analysis.

A sample was taken from the blue wrap, at the edge of the painting, to avoid damage to a central area. The cross-section was analysed by SEM-EDS and FTIR microscopy to collect information on the ground and pictorial layers. Additionally, a sample of the wooden panel was collected in order to identify the type of wood by means of optical microscopy.

5.4.4 Results and discussion

The analysis of a sample from the support identified oak as the wood species used for the panel, which is a type of wood widely used in North Europe, while poplar was mostly used in Italy.

The pictorial sample collected on the blue was analysed in cross-section (Figure 5.12). The ground layer, applied between the support and paint layers, *circa* 170 μm in thickness, is composed of three layers, all quite homogeneous. FTIR analysis showed that the layers are composed mainly of calcium carbonate (Figure 5.13). The organic binder is characterised by weak absorptions in the range 2930-2850 cm^{-1} and the band at 1713 cm^{-1} is associated to free fatty acids; a weak broad band around 1580 cm^{-1} is related to calcium carboxylates [28]. In order to establish the origin of the artwork, the presence of calcium carbonate is relevant: the use of calcium carbonate instead of gypsum indicates that this is not an Italian technique, but rather of northern European derivation [29, 30]. The composition of the preparatory layer is in fact generally determined by local custom rather than by other parameters [20].

Moreover, the blue wrap was investigated by SEM-EDS, finding Cu as main element, possibly associated to different pigments, but distinctively identified by FTIR microscopy as azurite (Figure 5.14). Pb is also detected by SEM-EDS and likely linked to lead white. The FTIR absorptions in the range 2925-2850 cm^{-1} are related to aliphatic CH (and therefore to the presence of an organic material) and the band around 1710 cm^{-1} is associated to free fatty acids, due to drying oil degradation.

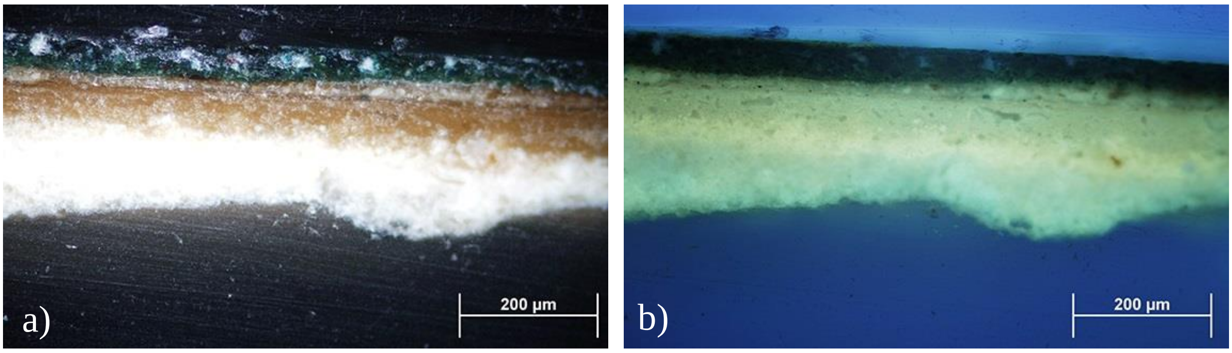


Figure 5.12. Cross section of the blue sample, a) visible light and b) UV.

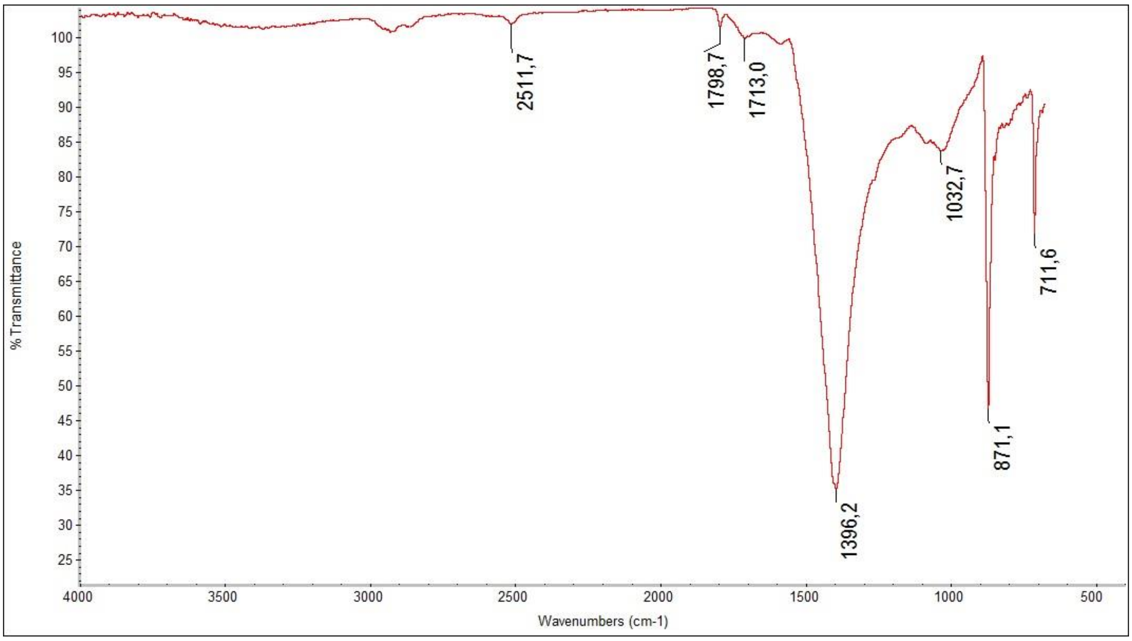


Figure 5.13. FTIR spectrum collected on the ground layer. Bands at 2511, 1799, 1396, 871, 712 are related to calcium carbonate.

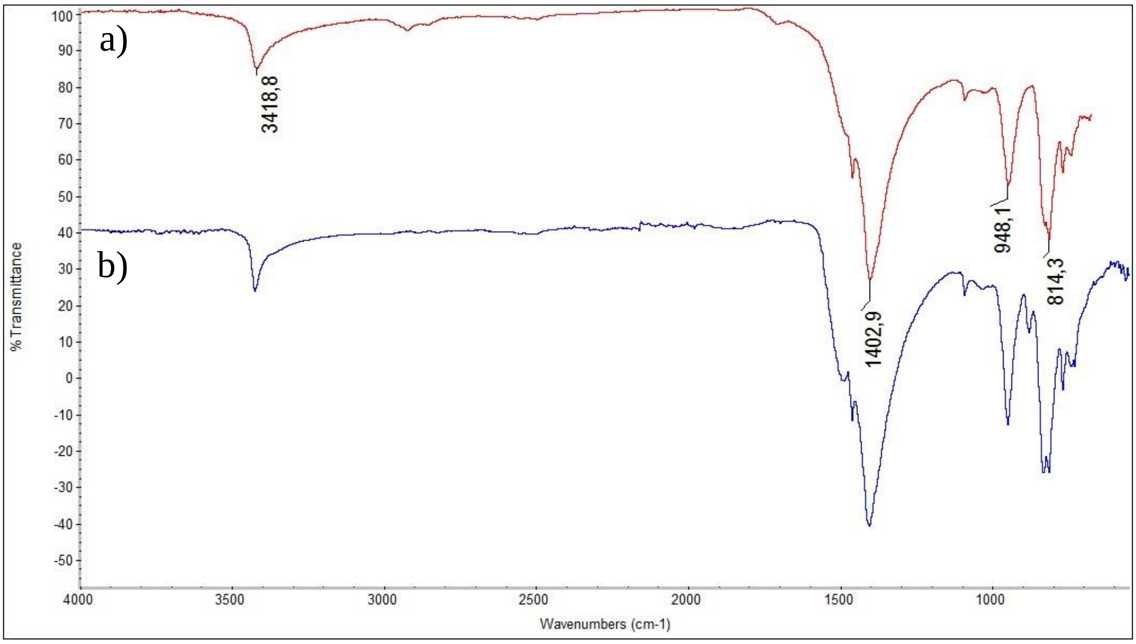


Figure 5.14. a) FTIR spectrum collected on the blue layer of the sample, b) standard of azurite.

5.4.5 Conclusion on the *Columbine*

Following the identification of a chronological and geographical settings by means of scientific analysis, which found the beginning of 17th century and North Europe as period of time and place of creation, the painting under study was excluded as a possible replica made by Melzi. It is therefore one of the copy based on the model proposed by Melzi as Columbine; further studies may identify a possible name of a copyist. At the end, a geographical context was identified and a new chronological range was proposed, changing the information previously associated to this painting.

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Chapter 6

Unknown paintings

6 Unknown paintings

The fortuitous discovery of a painting is probably not a rare scenario - the unveiling of new artworks appears often in the news[19]. These objects do not present any sort of documentation and do not show any attribution, thus their study relies upon gathering the widest possible body of information, applying a wide range of techniques to unveil every small detail which may be crucial for the classification of the artworks.

Accidentally discovered compositions are also found with the help of analytical techniques; for instance when an earlier painting is covered by a later one, thus it is not visible to the naked eye as it lies beyond the painted surface [1–3]. A copy of the famous *Mona Lisa* by Leonardo da Vinci illustrates this point – through X-ray radiography it was found that the artwork has been painted over an earlier composition: another artwork depicting a man was clearly discerned underneath (see paragraph 6.1). The investigation of this artwork paves the way towards the use of a methodology based on a wide set of combined techniques for the characterisation of materials and painting techniques, in conjunction with stylistic and documentary studies, to gather insights on both artworks and provide a classification of the object.

However, probably the most common case of unknown paintings is when an artwork is found not to be compatible, following an initial series of analyses, with what was originally expected, it is therefore necessary to classify the object into a new category (see paragraph 6.2). For instance, the *Paysage de montagne* painting already discussed in previous chapters was found incompatible with the attribution to the painter Ruyscher, who lived in the 17th century. Non-invasive analyses found the presence of titanium over the entire surface, suggesting the use of titanium white and thus moving the date of creation to the 1920s. As the attribution to Ruyscher is disproved, the focus becomes the identification of the materials and their contextualisation, so as to understand the nature of the object.

Clarifying the reasons behind undertaking an investigation is possibly the main question that guides the choice of a methodology, to deliver a comprehensive project which is able to satisfy all the demands and thus produce all the benefits. The scope of the work is then to understand what the essential means to answer the questions are, and define what happened to the painting during its

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[19] http://www.ansa.it/sito/notizie/cultura/2016/04/12/arte-un-presunto-caravaggio-ritrovato-in-soffitta-francese_7dbda616-02a7-4e54-9291-20e78c48b090.html; https://www.varesenews.it/2018/07/scoperto-un-de-chirico-nascosto-un-secolo-un-altro-quadro/731483/; https://www.finestresullarte.info/flash-news/3441n_svelato-secondo-dipinto-nascosto-santa-caterina-alessandria-artemisia-gentileschi.php (web pages accessed on July 2019).

history. Therefore, the team that will carry out the project, a timeframe and the methods and techniques to be applied to provide the required information should be defined at the beginning.

The analytical protocol in the case of an unknown painting comprises a set of combined techniques, from non-invasive to micro-invasive and micro-destructive. Integration of the findings with stylistic and documentary research is then mandatory to narrow down the results and possibly identify the period of execution and the possible artist.

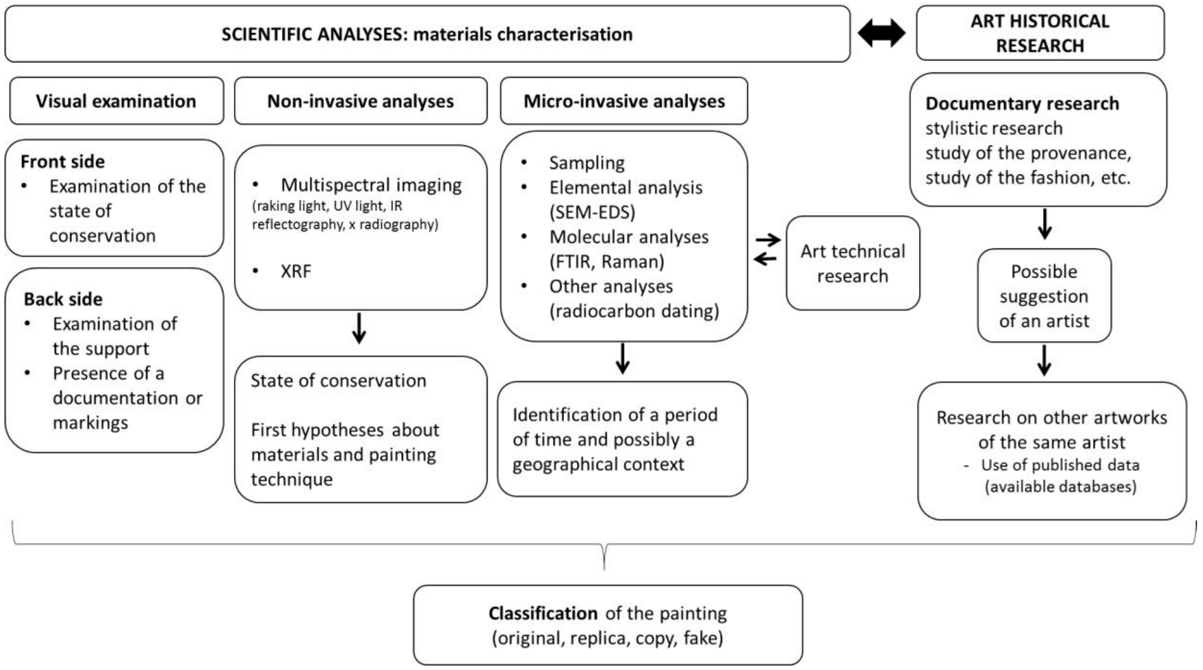
A close visual examination of the painting is the first step to undertake, both on the surface and the reverse. Any sort of documentation or markings can then be highlighted, such as inscriptions, seals or signatures. Professionals, such as conservators, initially carry out an investigation of the painted surface, to define the presence of retouched areas or the readability of the *craquelure*. Hypotheses as to the period and/or the style of the artwork can also be suggested at this stage, so to propose an attribution.

Non-invasive analyses assess the condition of the object and give a first indication as to the materials used. Multispectral imaging helps in the documentation of the object, as retouched areas, the presence of underdrawings and other features can be detected by means of the different lighting sources. With elemental and/or molecular analyses then carried out on the main colours of the surface a possible first identification of the pigments present is provided.

When possible, collecting a few samples to embed in cross-sections – after this first series of analyses, which will have indicated optimal sampling locations – is useful to furnish new and valuable data.

To classify the unknown painting, the first step requires the identification of the period in which the artwork can fall. Several features should be taken into consideration, such as the support, ground and pictorial layers. These characteristics also help in narrowing down a geographical context, especially for historic paintings where the materials, at least for the ground, would have been locally sourced.

Once the chronological frame and possibly the geographical context are identified, the suggestion of an artist to attribute the painting can be carried out by other professionals, for example conservators or art historians, and the attribution can be checked using scientific analyses and available shared databases.


SCIENTIFIC ANALYSES: materials characterisation
ART HISTORICAL RESEARCH
Visual examination
Non-invasive analyses
Micro-invasive analyses
Front side
Examination of the state of conservation
Back side
Examination of the support
Presence of a documentation or markings
Multispectral imaging (raking light, UV light, IR reflectography, x radiography)
XRF
State of conservation
First hypotheses about materials and painting technique
Sampling
Elemental analysis (SEM-EDS)
Molecular analyses (FTIR, Raman)
Other analyses (radiocarbon dating)
Identification of a period of time and possibly a geographical context
Art technical research
Documentary research
stylistic research
study of the provenance,
study of the fashion, etc.
Possible suggestion of an artist
Research on other artworks of the same artist
Use of published data (available databases)
Classification of the painting (original, replica, copy, fake)

6.1 Mona Lisa

6.1.1 Introduction

The *Mona Lisa* painting in a private collection portrays a copy of the well-known masterpiece by Leonardo da Vinci. The pivotal role of X-ray radiography provided new insights into this artwork, revealing a hidden painting, turned upside down and depicting a man, beneath the visible Mona Lisa (Figure 6.1).

The main purpose of this research is to develop an understanding on paintings from a scientific point of view, characterising materials and techniques. In particular, the study aims to address diverse research questions. The peculiar discovery of the hidden portrait offers the opportunity to study an unknown painting of which no information was available. Therefore, a methodology can be applied to understand the chronological range in which was executed, possibly identify a geographical context and finally suggest an artist; in this way the object will be classified. At the same time, the investigation of the materials of the Mona Lisa gathered new insights about this upper painting, delivering information about a date of creation.

The research on this artwork provided an important contribution to advance knowledge on the investigation of unknown paintings, and suggested research based on micro-invasive analyses to answer questions about its nature.

6.1.2 Materials and Methods

The previous investigation on the Mona Lisa through X-ray radiography allowed to find out the presence of the hidden portrait of a man; the importance of a non-invasive investigation at the beginning of every scientific study is thus reinforced as fundamental part of the research.

XRF analysis was carried out in order to have a first insight into the pigments present and, at the same time, find locations to collect samples. Cross-section analyses was indeed necessary to characterise both paintings, gathering information on every analysed layer. In particular, the samples were collected superimposing the visible image of the Mona Lisa and the X-ray radiography of the hidden man, in this way the chosen samples include information about diverse parts of the lower painting (the background, the clothing of the man, the flesh tones) and at the same time about the various colours of the Mona Lisa. Fragments were documented by stereo-microscopy on both front and back side and, after embedding, with an optical microscope in visible and UV. Then, they were analysed by SEM-EDS and Raman microscopy in order to exhaustively characterise the materials.

6.1.3 Results and discussion

XRF was performed on the main colours present in the painting. Due to the complexity of the artwork, several spots were analysed for each area, as the sky, the flesh tones and the clothing of the Mona Lisa, in order to find out information about the hidden portrait (Figure 6.1).

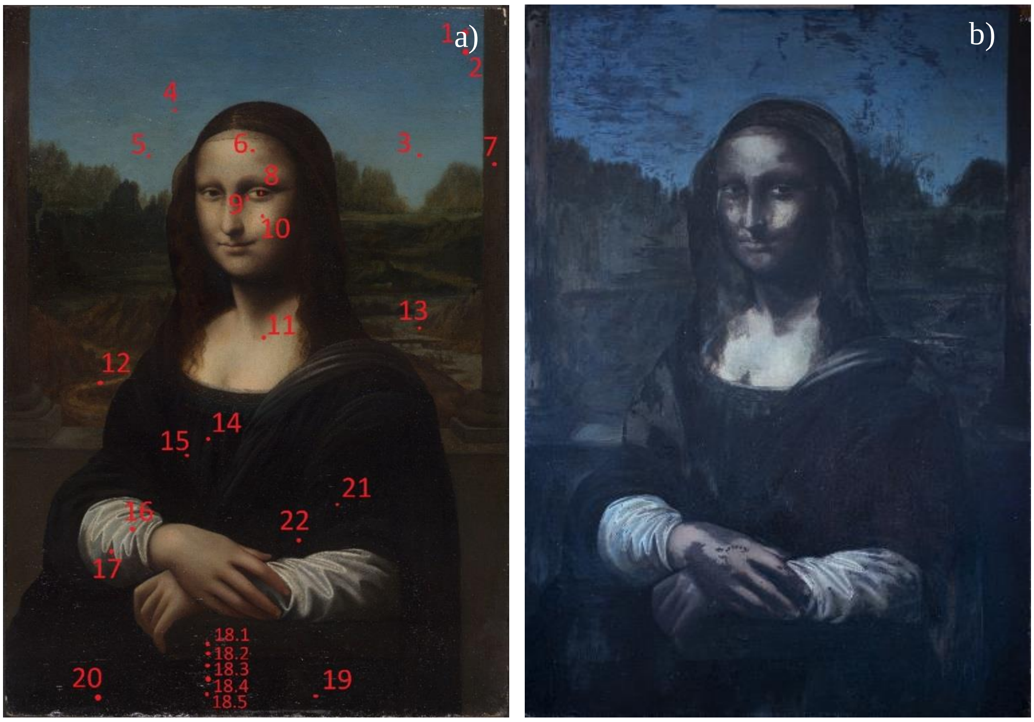


Figure 6.1. a) The Mona Lisa painting with the measured XRF spots; b) the painting under UV.

In the blue of the sky no element associated to a blue pigment has been detected, as copper (likely associated to azurite) was found only in a small amount in comparison to other elements and thus is considered an impurity; therefore the presence of ultramarine blue or organic pigments, not detectable with XRF as made by light elements, is suggested.

The analyses on the flesh tones found out Pb as likely lead white, Fe and small amounts of Mn related to ochres and/or earth and umber pigments.

The robe of the Mona Lisa was investigated on several spots and the interpretation of pigments was based on Fe, as likely ochres and/or earth and umber pigments due to the presence of Mn, and P, possibly related to bone black. In particular, the measured spots numbered from 18.1 to 18.5 were chosen as they correspond to the face of the man underneath; the only difference in comparison to the other spots measured on the robe was the identification of Hg, likely linked to vermilion. This pigment is then suggested to be present in the hidden painting.

The presence of tin and/or antimony, found on each analysed spot, was of difficult interpretation due to the low intensity of these peaks. A further investigation was then essential to clear this aspect, as diverse yellow pigments based on lead, tin and antimony exist and were used at different times in art history.

The investigation on the face, robe and background gathered also information about the restoration materials, as Fe, Ti and Cr were detected on a few spots. In particular, the presence of titanium is likely associated to titanium white and Cr can be present both in yellow or green pigments.

Eight samples were then collected from different areas of the painting in order to gain information both on the hidden portrait of a man and on the Mona Lisa (Figure 6.2, Table 6.1). The two paintings will be discussed separately (Table 6.2).

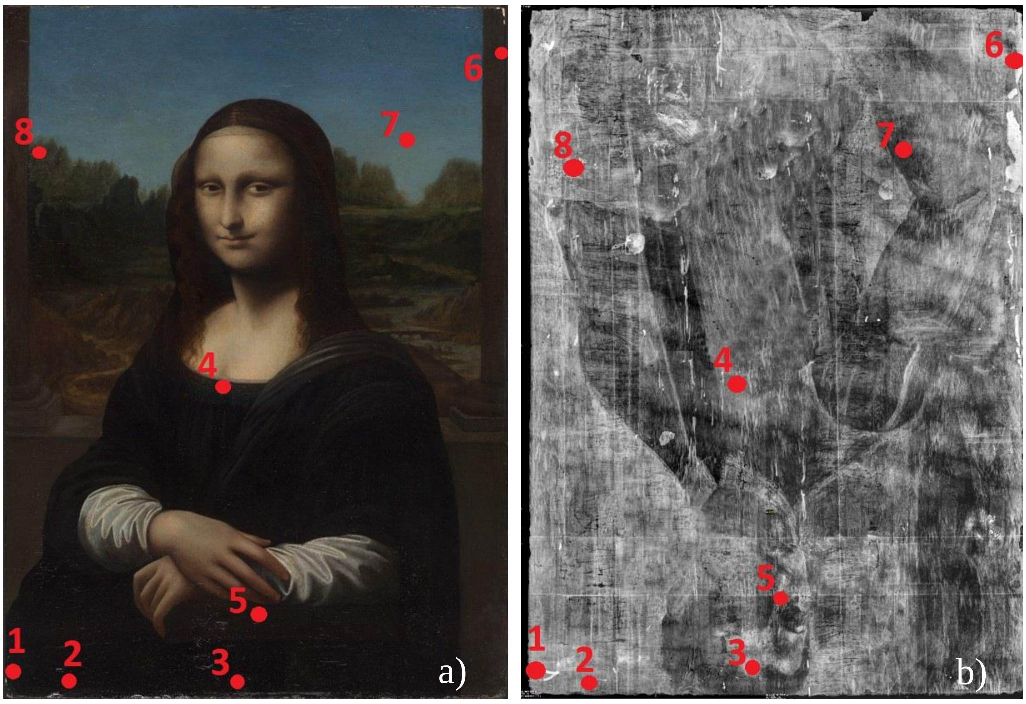


Figure 6.2. a) Sampling spots on the Mona Lisa painting and b) the corresponding spots on the Man painting.

Table 6.1. List of the samples collected from the artwork. A comparison is expressed between the area visible on the Mona Lisa and the suggested area on the hidden man.

Nr.	Colour visible on the Mona Lisa	Area on the hidden man
1	Black dress	Background
2	Black dress	Background
3	Black dress	Flesh tone (forehead)
4	Yellow embroidery of the dress	Dress
5	Black dress	Flesh tone (nose)
6	Dark column	Background / drapery
7	Blue sky	Dress
8	Green trees	Dress

6.1.4 Hidden portrait of a man

Ground layer. Three samples were collected up to the original ground layer (nr. 2, 5 and 6), allowing to characterise the preparation of the lower painting. The white ground is mostly made of calcium and sulfur, likely associated to calcium sulfate. A few grains are made of Sr, possibly associated to strontium sulfate, which is a mineral called celestine often found in gypsum as an impurity [4]. Raman analyses identify calcium sulfate anhydrous [5] for the peaks at 1159, 1129, 1017, 676, 629, 609, 417cm^{-1} (Figure 6.3). A ground layer based on calcium sulfate is typical of 16th century Italian grounds [6–8].

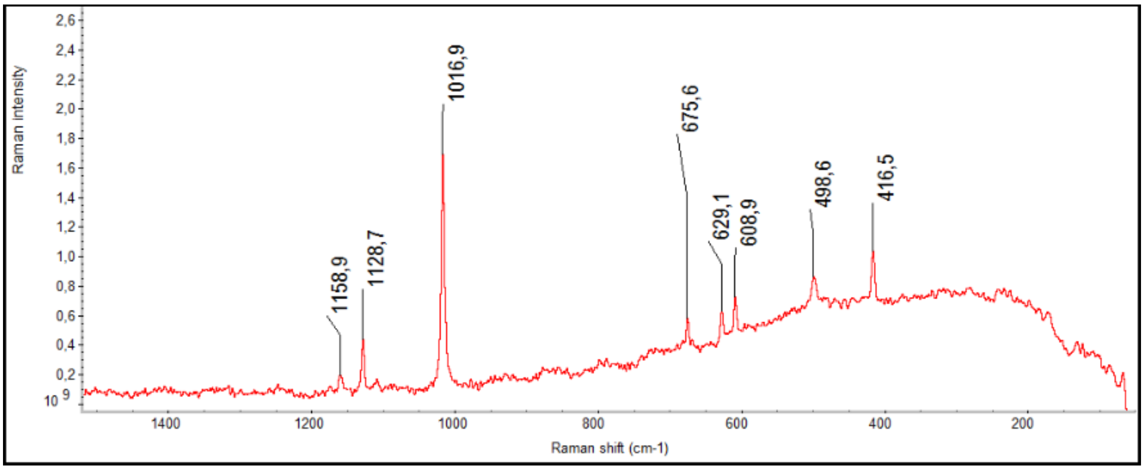


Figure 6.3. Raman spectrum on the white ground.

Grey background. Samples 1 and 2 were collected on the area corresponding to the background of the hidden painting.

The first dark grey layer visible on both samples is made of Pb as likely lead white, and Fe and Mn associated to earth and umber pigments. Raman analysis identifies bands at 1330 and 1595 cm^{-1}, related to carbon black.

Sample 1 shows at least 3 grey layers, starting from a light grey one, laid on top of the ground, and then darkening the colour with a greater amount of carbon-based pigments.

Black dress. Samples 4, 7 and 8 are collected from the robe of the hidden man. The cross-sections show a first layer of black colour. Raman bands at 1330 and 1595 cm^{-1} identify carbon black; in sample 8 the P peak in SEM-EDS spectra hypothesises the presence of bone black. This technique also found Pb and Fe in all the samples, likely associated to lead white and ochres, respectively.

Flesh tones. Samples 3 and 5 are collected on the corresponding flesh tones of the hidden painting: on the forehead and the nose, respectively. The pink layers contain almost the same elements, with Pb as predominant element, likely linked to lead white; blue grains contain copper, likely related to azurite, while red grains are both Hg-based, likely related to vermilion, and C-Al-based, and are thus probably red lakes. Raman analysis confirms the presence of vermilion (253, 341 cm^{-1}).

Sample 3 shows a complex stratigraphy (Figure 6.4). On top of the two original flesh tones layers (nr. 1-2), an organic layer is detected, (nr. 3) possibly a varnish, and a pink layer is visible on top of that (nr. 4). The grains size of this layer is finer in comparison to the two lower layers, and the composition is also different. By SEM-EDS analyses, Pb, Fe and Hg are detected, and the blue grains are made of Na, S, Al, Si, Ca, which are the elements related to ultramarine. Raman analysis confirms the presence of ultramarine (545 cm^{-1}), red ochres (226, 294, 413 cm^{-1}) and vermilion (253, 342 cm^{-1}).

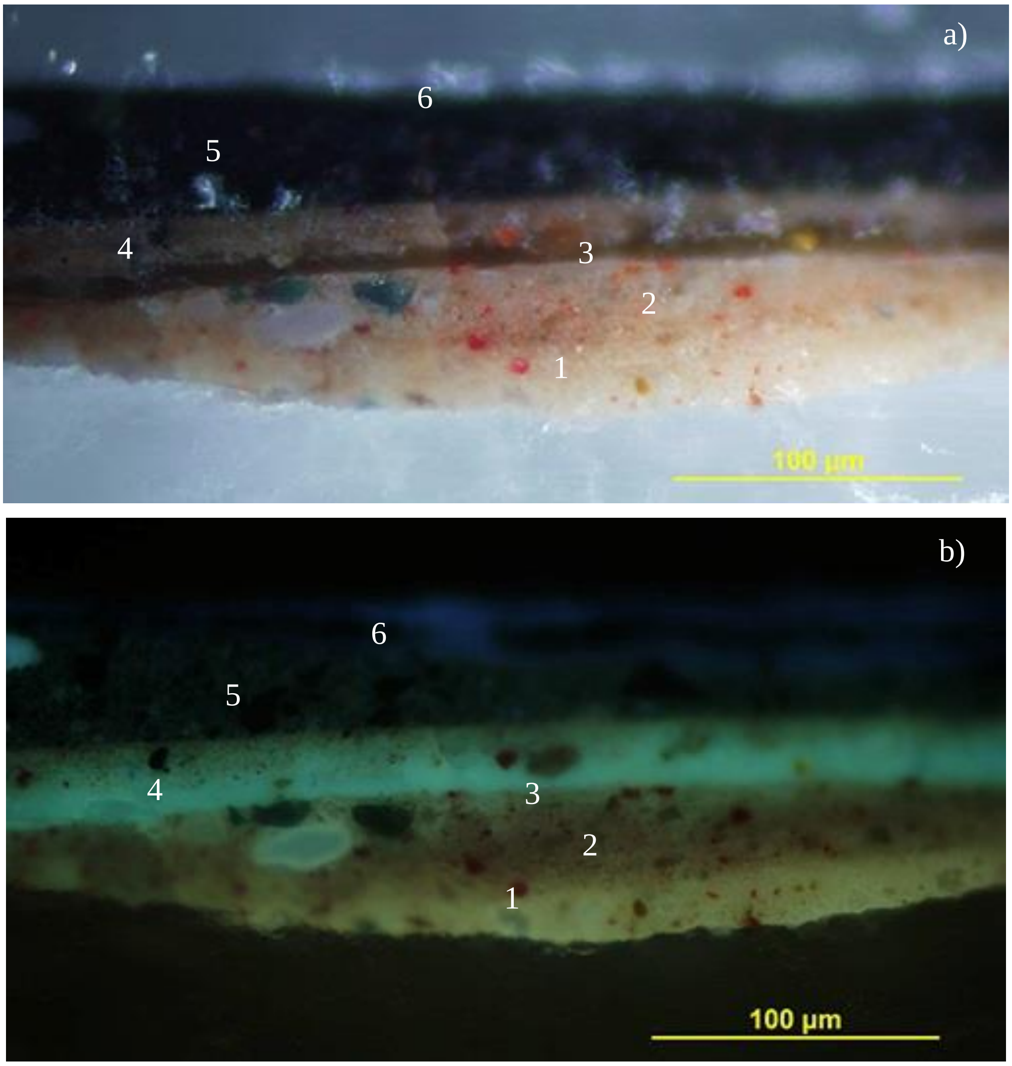


Figure 6.4. Cross section of sample 3, a) visible light and b) UV.

Blue decoration on the background. Sample 6 was collected at the bottom left of the hidden man (top right of the Mona Lisa) and it corresponds to a blue ornament, such as a drapery. The first pictorial layer (Figure 6.5, nr. 1) appears grey and it is scattered with very fine grains. The mixture contains mostly lead as likely lead white, and a small amount of copper is possibly related to green or blue pigments. The presence of carbon black is not excluded.

The second pictorial layers (nr. 2) is blue and large and coarse blue grains are visible. The presence of Pb is likely associated to lead white, and the Cu-based blue grains are identified by Raman as azurite (Figure 6.6).

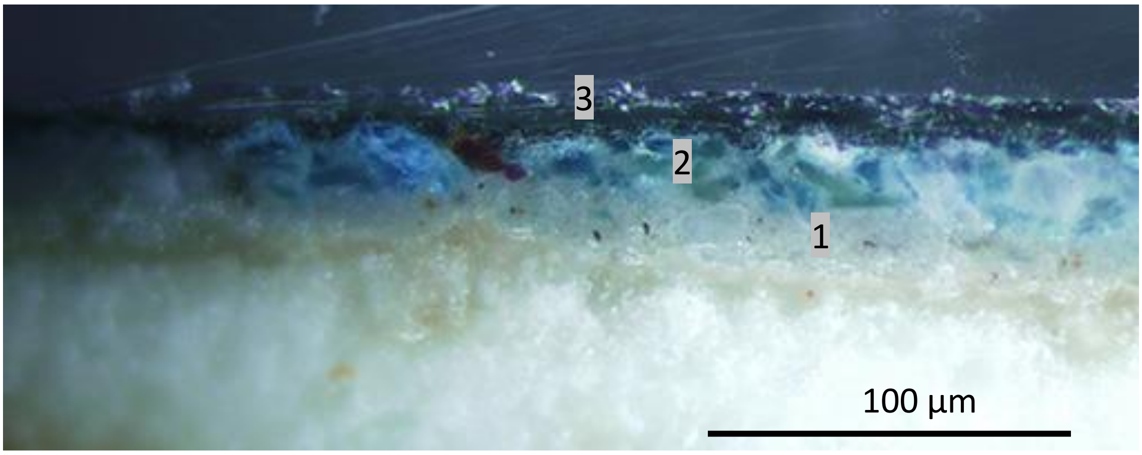


Figure 6.5. Cross section of sample 6.

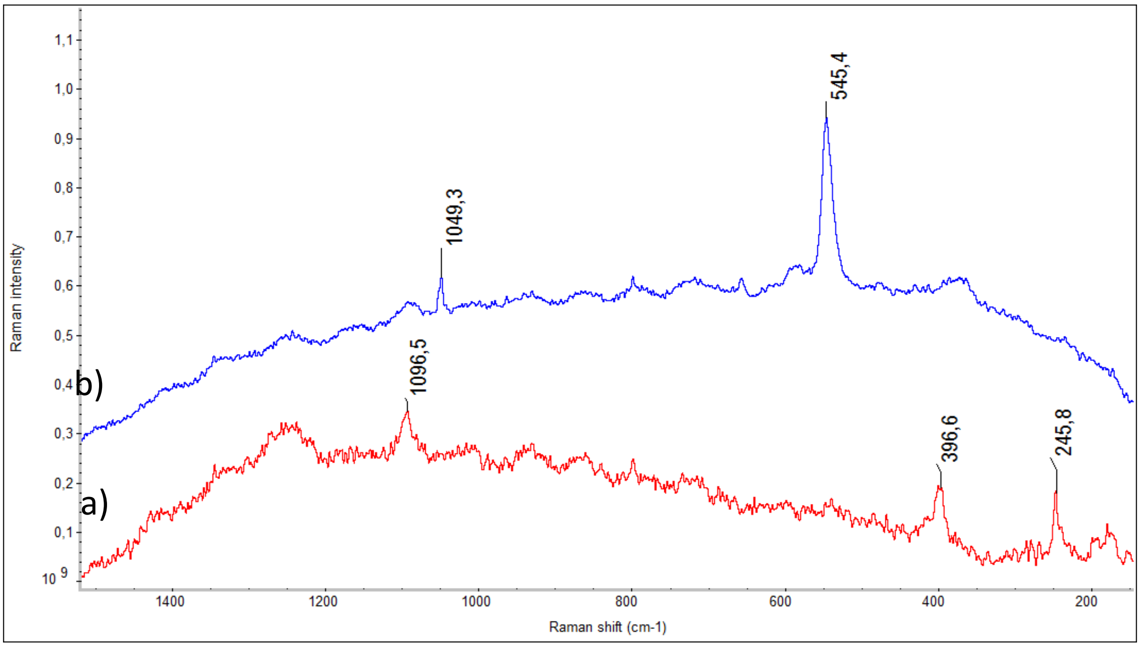


Figure 6.6. Raman spectra collected on a) sample 6 and b) sample 7; azurite and ultramarine are detected, respectively.

6.1.5 Mona Lisa painting

The second upper painting depicting Mona Lisa seems to be painted directly on top of the first one, as no separation layer is visible in the cross-sections. The exception is sample 3, which shows a complex stratigraphy and an organic layer between the original part and the repainted one.

Black dress. Samples 1, 2, 3 and 5 are collected on the black dress of the Mona Lisa. Samples 2 and 3 show a black layer containing P, likely associated to bone black, Fe to ochres and Hg to vermilion. Pb and Sb are likely associated to a yellow pigment, such as Naples yellow.
Samples 1, 3 and 5 show a different composition of the black colour: Raman bands at 1330 and 1600 cm^{-1} identify carbon black and the one at 142 cm^{-1} is characteristic of titanium white in the anatase form. SEM-EDS spectra show the presence of Cr, probably associated to green pigments as Pb was not found, Cu, related to green or blue pigments, Fe, likely related to ochres and Ca, associated to calcium carbonate or sulfate.
The heavy retouch of the painting at a later time is responsible for the different composition of the black layers, as clearly visible under UV. Therefore, the first mixture, made of bone black, ochres and vermilion, could be related to the Mona Lisa painting, while the second mixture, mostly containing carbon black and titanium white, was used during the restoration intervention. In particular, the presence of titanium white in the anatase form allows to date this layer at least during the 1920s [9].

Yellow embroidery. The embroidery of the dress consisted of a yellow decoration applied on a dark blue background. The first blue layer is made of ultramarine, identified by Raman and likely to be artificial due to the fine grains size. The yellow layer will be thoroughly described as follows, and on top of that, a layer with a red UV fluorescence is present, thus it is suggested to be a red lake.
The yellow layer mostly contains Pb and Sb (Figure 6.7), and a few grains are made of Fe, possibly associated to ochres. The Raman band at 130 cm^{-1} (Figure 6.8) could correspond to Naples yellow [10], but the Pb-O stretching mode in this region is affected by several factors and thus not diagnostic. For instance, the broad shape of the peak may also suggest the presence of the ternary lead-tin-antimony oxide [11, 12], as the characteristic doublet at 125-142 cm^{-1} present in this compound sometimes is not entirely resolved. Moreover, the band at 130 shifts from 140 to lower frequencies in compounds with silica, and that is also corroborated by the presence of the band at 658 cm^{-1} [12, 13]. However, the SEM-EDS spectrum of the yellow sample only shows the presence

of Pb and Sb (Figure 6.7). Further investigation are required in order to understand the amount of tin present, if any, and therefore the nature of the pigment used in this layer.

Bands at 510 and 656 cm^{-1} are also related to lead antimonate, and the one at 656 increases with a higher amount of the Pb:Sb ratio [11].

Analyses on orange grains (spectrum ii on Figure 6.8g) detected lead antimony oxide (Naples yellow), as the bands at 142, around 330 and 512 cm^{-1} demonstrate [12].

The band at 973 cm^{-1}, present on the whole layer (Figure 6.8e), was also observed on some 17th paintings, and it may be related to lead sulfates [11].

Naples yellow was highly popular in Europe between approximately 1750 and 1850, and then was gradually replaced by other pigments [14]. The ternary Pb-Sn-Sb oxide originates from the glass manufacture; it was systematically used in 17th paintings, especially in the Rome area [15], other examples were found in 18th and 19th Mid European paintings [16]; this pigment was also used until the 19th century.

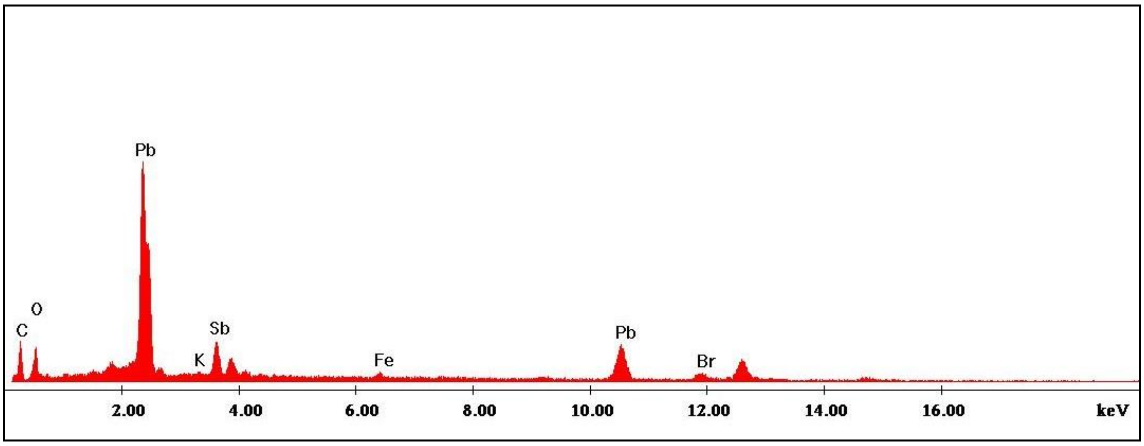


Figure 6.7. SEM-EDS spectrum collected on a yellow grain.

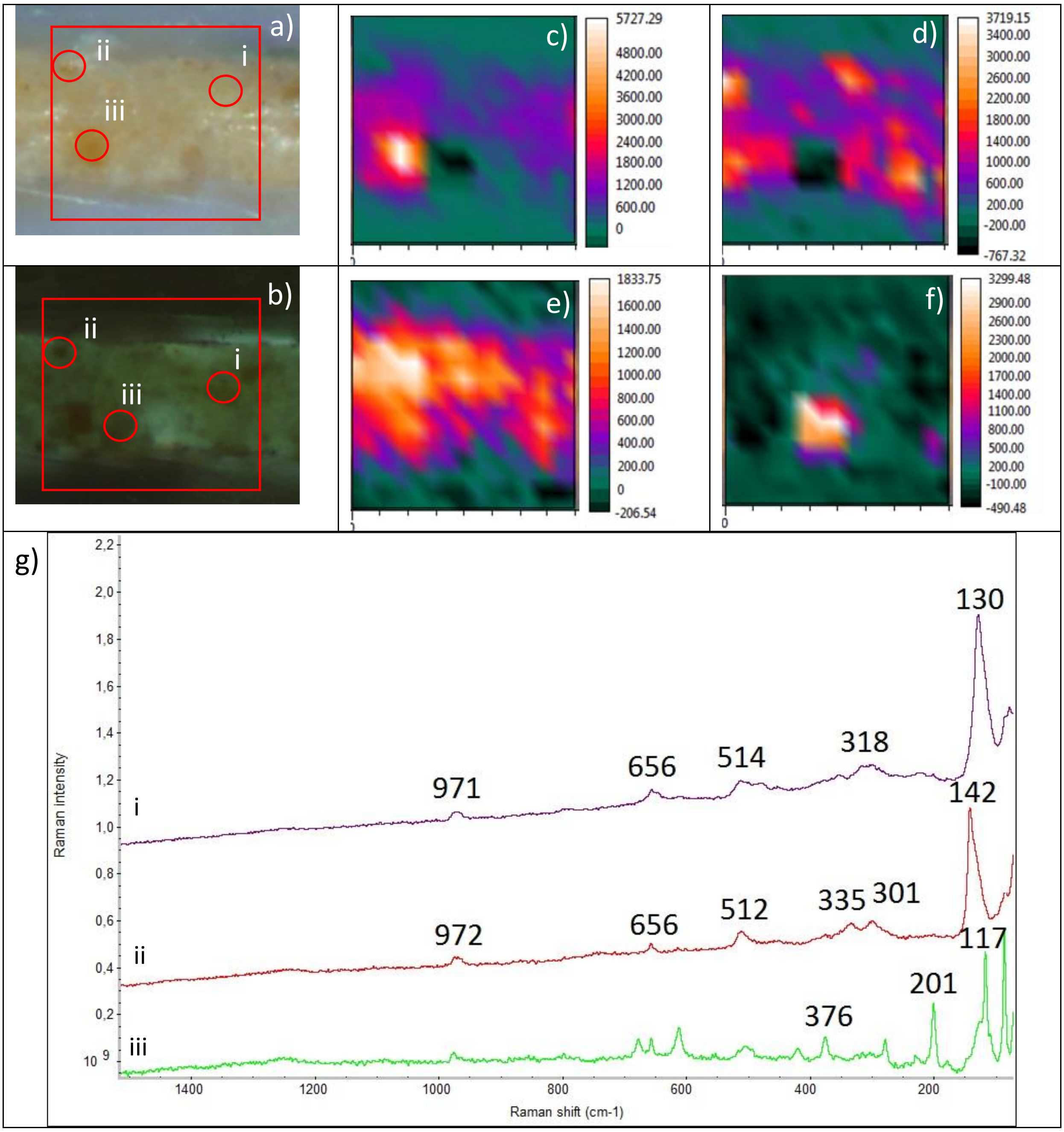


Figure 6.8. a) Cross-section of the yellow sample, the red square indicates the area of the Raman mapping, the spots of the extracted Raman spectra are indicated as circles; b) sample under UV. Raman maps in false colour obtained mapping the band at c) 130 (125-135) cm^{-1}, d) 658 (650-670) cm^{-1}, e) 975 (970-980) cm^{-1}, f) 118 (115-120) cm^{-1}; g) Raman spectra extracted from the map, collected on the spots indicated in a-b.

Background/sky. Samples 7 and 8 were collected on the sky of the Mona Lisa. The blue layers contain round blue particles, identified by Raman as ultramarine blue (545 cm^{-1}) (Figure 6.6). The characteristic shape of the grains allows to suggest that it is a synthetic pigment [17–19] (Figure 6.9). The band at around 1050 cm^{-1} is related to lead white. Yellow particles consist of Pb and Sb and show a band at 130 cm^{-1}, associated to Naples yellow.

The last pictorial layer of sample 8 is of green colour, associated to the trees on the background. The presence of Cr-based compounds allows to hypothesise the use of Cr oxides as green pigments. Ti, linked to titanium white, and Pb, as lead white or Cr yellow, are also detected.

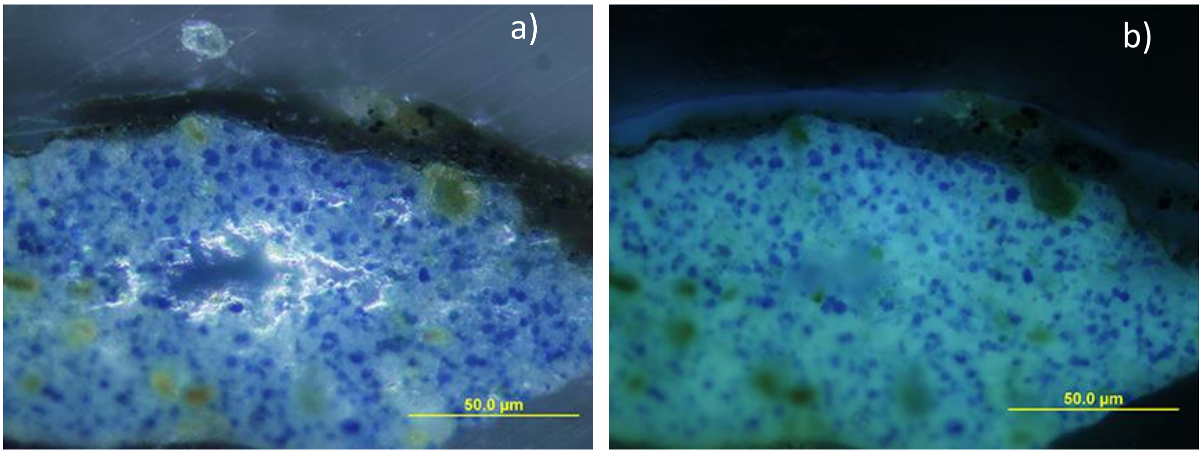


Figure 6.9. Cross-section of sample 8, a) visible light and b) UV. The round shape of the blue crystals may be related to synthetic ultramarine.

6.1.6 Conclusion

The essential role of non-invasive analyses is undoubtedly evident in this research. X-ray radiography was indeed able to detect a hidden painting underneath the visible Mona Lisa, opening the study to the investigation of this unknown object. UV fluorescence was also necessary to identify retouched areas – important to avoid during the analyses – this painting has been heavily retouched over time. Meanwhile, sampling was considered crucial to characterise both paintings.

The first, lower painting, portraying a man (discovered by X-ray radiography), presents a ground layer made up of calcium sulfate in the anhydrite form ($CaSO_4$). It is visible as a preparation layer in three samples (nr. 2, 5, 6) but it is assumed to be laid over the entire painted surface.

The flesh tones of the man were studied on the forehead and nose (samples 3 and 5): a lead white matrix is scattered with azurite, vermilion and red lakes.

The background appears to be grey (samples 1 and 2), and it is made mostly of carbon black, lead white and earth pigments, with silicates as extenders.

The clothing (samples 4, 7, 8) is a black colour - bone black, ochres and lead white were detected.

Sample 6 gave information on the edge of the painting, where blue drapery appears to be painted. The area is made up of two layers of azurite mixed with lead white, the first one with fine grains also mixed with carbon black, and the second with coarse grains.

The white calcium sulfate ground was common during the 14th to the half/third quarter of the 15th century in Italy. The identified pigments are all compatible with this timeframe.
Therefore, the hidden man painting shows a possible date of execution between the 14th century and the half/third quarter of 15th century. Scientific investigation follows the stylistic study of the clothing and hair of the man, which resemble the fashion of the Tuscany area of 1545-55[20].
A separation layer between the two paintings is not visible. Only sample 3 shows an organic layer between the original painting and a possible retouch.

Various colours of the Mona Lisa were also characterised and several pigments were identified, including bone black, ochres, earth and umber pigments and vermilion. In addition, finding specific pigments allowed proposal of a dating range. For instance, as ultramarine blue in the synthetic form (detectable by the round shape of the grains) was found on several areas of the painting, for example the sky and the dress, a *terminus post quem* was identified, meaning the painting was executed after at least 1828, the year of the commercialisation of ultramarine blue. The identification of Naples yellow suggests a *terminus ante quem*, as this pigment appears to be present in art history until the 19th century. For these reasons, the Mona Lisa can be dated from 1828 to the end of 19th century, and it is classified as a copy.

In some samples (nr. 2, 3, 5, 8) there is a final black layer made mostly of carbon black mixed with chromium-based green pigments, lead white, ochres and titanium white. The latter has been in commercial production since 1920s, therefore this layer can be associated to retouch materials used during a restoration intervention made at least at the beginning of the 20th century.

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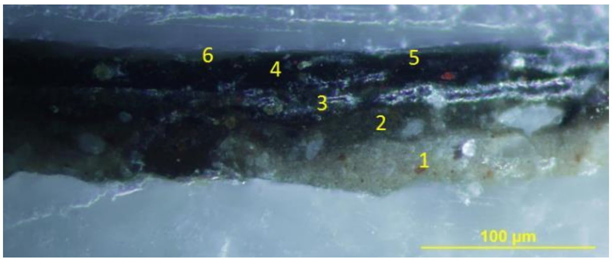
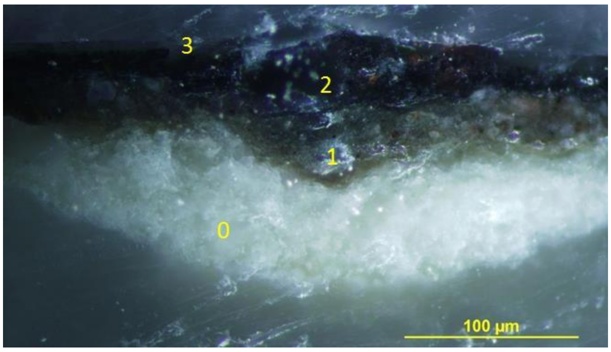
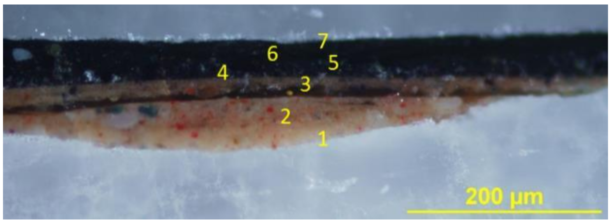
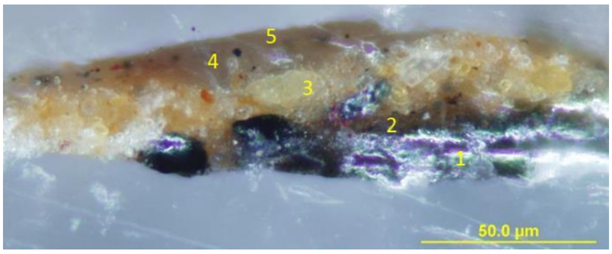
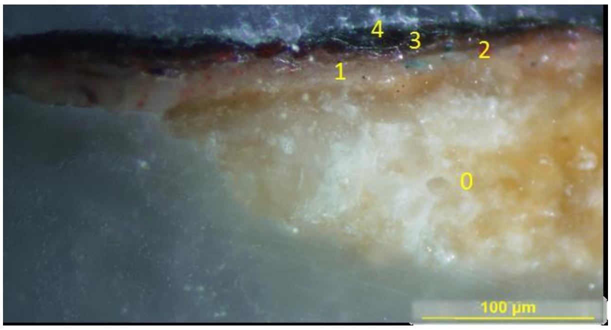
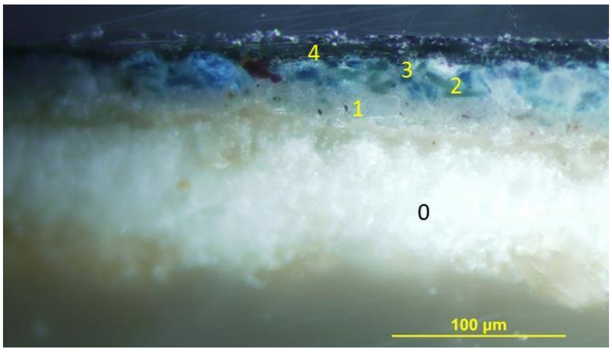
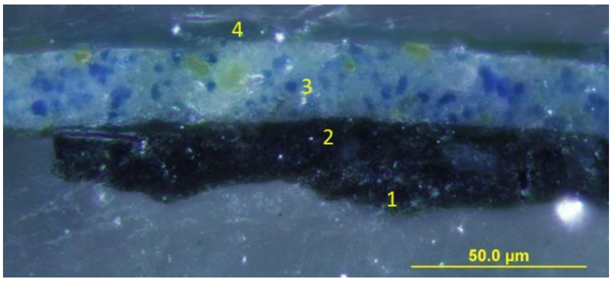
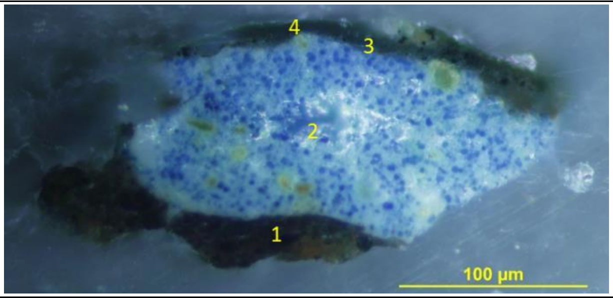
[20] Investigation on the fashion was carried out by art historian Elisabetta Gnignera (report not shown here).

Table 6.2. Summary of the result; for each cross sections the layers are numbered and the identified pigments are expressed.

N	Cross-section image	Identified pigments
1		6. Varnish 5. Varnish 4. Bone black, ochres, vermilion, Naples yellow 3. Bone black, lead white, ochres, calcium carbonate, silicates 2. Lead white, earth pigments, calcium carbonate, silicates, carbon black 1. Carbon black, lead white, earth pigments, calcium carbonate
2		3. Varnish 2. Carbon black, chromium-based green pigments, copper-based pigments, ochres, calcium carbonate/sulfate, titanium white (anatase) 1. Carbon black, lead white, earth pigments 0. Calcium sulfate (anhydrite)
3		7. Varnish 6. Carbon black, chromium-based green pigments, copper-based pigments, ochres, calcium carbonate/sulfate, titanium white (anatase) 5. Varnish 4. Calcium carbonate, lead white, bone black, alumino-silicates, ochres, earth pigments, vermilion, Naples yellow 3. Lead white, ultramarine blue, earth pigments, bone black, alumino-silicates 2. Lead white, azurite, vermilion, ochres 1. Lead white, yellow ochres, azurite, vermilion
4		5. Varnish 4. Red lakes 3. Naples yellow, bone black, lead white, red ochres 2. Ultramarine blue (synthetic), red ochres (rare) 1. Carbon black, lead white, red ochres

5		4. Varnish 3. Carbon black, chromium-based green pigments, copper-based pigments, ochres, calcium carbonate/sulfate, titanium white (anatase), bone black, alumino-silicates 2. Ochres, Naples yellow, earth pigments, ultramarine blue, bone black 1. Lead white, azurite, vermilion, red lakes 0. Calcium sulfate (anhydrite)
6		4. Varnish 3. Naples yellow, bone black, silicates, red ochres 2. Azurite, lead white, red ochres (rare) 1. Azurite, lead white, carbon black 0. Calcium sulfate (anhydrite), celestine
7		4. Varnish 3. Ultramarine blue (synthetic), Naples yellow, lead white 2. Carbon black, lead white, ochres, Na,Mg alumino-silicates 1. Carbon black, lead white, Na,Mg alumino-silicates, earth pigments
8		4. Varnish 3. Lead white, ochres, chromium-based pigments, alumino-silicates, titanium white (anatase) 2. Ultramarine blue (synthetic), Naples yellow, lead white 1. Carbon black, lead white, ochres, Na,Mg alumino-silicates, bone black, silica

6.2 Paysage de montagne

6.2.1 Introduction

The painting was examined in previous chapters (paragraphs 4.1.2 and 5.1) as it shows an inscription with the name of the artist on the back and therefore was analysed to find a chronological correspondence with the 17th century. As non-invasive analyses detected elements related to pigments belonging to the 19th – 20th century, the attribution to this artist was reconsidered. In order to understand the nature of the object being studied, further micro-invasive analyses were carried out combining radiocarbon dating[21] and materials characterisation. In addition, a documentary research[22] on this minor artist of the 17th century allowed to contextualise the data and shed a new light on this artworks' history.

The painting in question was sold in 2012 in Cannes (Cannes auction, auctioneers: Nicolas Debussy and Carine Aymard, lot no. 26), with a certificate of authenticity from the Parisian expert René Millet testifying to its status as a work of Jan Ruyscher. In 2014 thanks to a scheduled restoration intervention, the restorer Suzanne Stocker hypothesized that the pigments were not from the 17th century, raising doubts about the attribution. In 2017 the artwork was examined by an art expert at the Lempertz auction house, who also suggested that it was a modern painting. The challenge of this research was objectively disproving that this artwork was one of the few original paintings made by Ruyscher and demonstrating that it is a copy in the manner of Ruyscher or a fake, possibly made after the discovery of this minor artist in 1932, thanks to the study carried out by Welcker, or after 1998, inspired by a Ruyscher's engraving conserved at the Rijksmuseum of Amsterdam.

6.2.2 Documentary research

Jan Ruyscher is considered one of the Little Dutch Masters of the 17th century, who is a category of artists still not well-known nowadays and thus their attributed artworks are only a few. Ruyscher was born in the Netherlands, possibly in Franeker, around 1625 and he was active in Amsterdam in 1645, where he might have been worked in Rembrandt's workshop [20, 21]. He was Hercule Seghers' pupil, as he was also called "Jan Ruyscher alias the young Hercules" [21]. His career was prestigious, as he worked in many courts, and possibly died approximately around 1675 [21]. Although his rich career, only a few paintings attributed to Ruyscher are known and even rarer engravings and drawings with his signature (*J. Ruischer, Iohannes Ruischer* or *Iohannes Ranscher*). After his death, his name was once remembered in 1721 [22] and then he was ignored until the

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[21] Radiocarbon dating analysis was carried out at the Laboratory of Ion Beam Physics, ETH Zurich.

[22] The research about the history of both painter and panting was carried out by Professor Eric Huysecom.

beginning of 20th century, when a private collector, Albertus Welcker, rediscovered Ruyscher and wrote a monography about this artist in 1932 [23]. This study will be edited in five parts in the Oud Holland journal between 1932 and 1936 [21, 24–27].

The discovery of paintings attributed to Ruyscher is therefore of utterly importance for unveiling this artist's technique, as he was an unknown artist until the 1930s.

6.2.3 Materials and Methods

Description of Paysage de montagne

This oil on panel (17 x 20.7 cm) depicts a valley among a rocky landscape, where a castle on a promontory is upon a village and three characters are visible on a tortuous path. The letters "Ra" are hardly visible at the bottom left, possibly related to a signature. The style of this artwork reminds of a Ruyscher's engraving conserved at the Rijksmuseum since 1816 (Inv. N° RP-P-OB-12.875), absent from the Wacker's catalogue. In 1998 the Bassenge auction house sold a second copy of this engraving (vente Bassenge - Berlin, 27-11-1998, N° 5403), unknown until then. Other elements, such as a high aerial perspective, the three characters lost in the landscape, the alternate light and shadow areas to create depth, are all present in Seghers' engravings and paintings.

Samples

Four samples were collected from the painting surface in order to characterise different colours: the blue of the sky (nr. 1), the brown of the landscape (nr. 2), the retouched green of the trees (nr. 3) and a green of the foliage (nr. 4). Sample nr. 3 was deliberately taken on a restoration area in order to gain information on the used restoration materials. Cross-sections were obtained by embedding the samples in KBr pellets, then polyester resin [28] and then analysed with SEM-EDS, FTIR and Raman microscopy.

From the wooden support seven samples for radiocarbon dating were collected and these were treated following conventional sample preparation procedures (see Chapter 2.2).

6.2.4 Results

Radiocarbon dating on the support

In the present case, the outer tree ring was determined to be 1661-1664 while the youngest 1730-1753 (2σ, 95% confidence interval), which implies that the tree was growing between the end of the 17th century up to mid-18th. Therefore, the uncertain dendrochronological dating is confirmed by wiggle-matching of ^{14}C dates.

Materials characterisation

The four cross-sections were characterised from the ground to varnish layer; the results are expressed in Table 6.3.

Ground layers. The ground of all the four samples consists of two white layers of similar composition. Titanium white is identified in the anatase form, mixed with barium sulfate and calcium carbonate (see below Figure 6.11). The latter is characterised by FTIR as calcite (~1410, 872 cm^{-1}), mixed with another type of carbonate with a predominant band at 1450 and a second one at 853 cm^{-1}, found in aragonite polymorph calcium carbonate [29–31], the absorption at 1470 is also related to aragonite [32] and the one at 1656 cm^{-1} can be associated to the C=O stretching vibration of carbonates [33] (Figure 6.10).

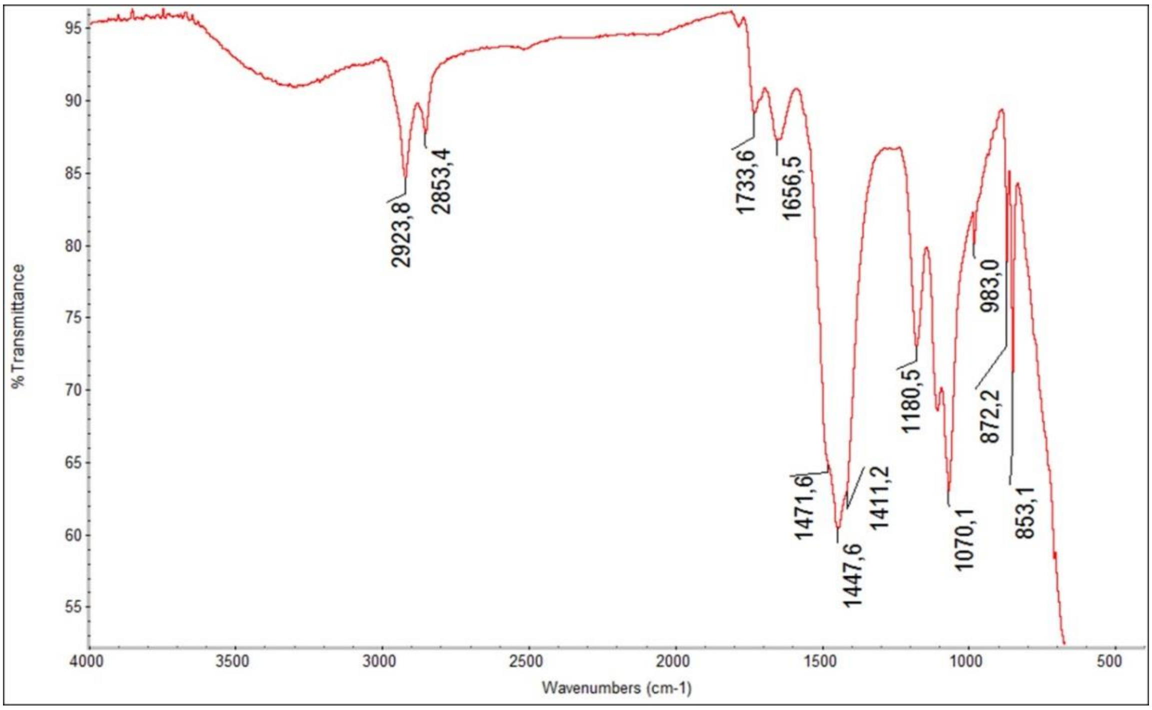

Figure 6.10. FTIR-ATR spectrum collected on the ground of sample nr.1.

Moreover, the binder is identified as a drying oil. The zinc peak in the SEM-EDS spectra can be associated to zinc oxide or zinc sulphide: the latter, together with barium sulfate, is characteristic of lithopone. The differentiation between the two Zn-based pigment was not trivial: the S peak detected in SEM-EDS that may help in distinguish between the oxide and sulfide form is also linked to barium sulfate, masking the possible presence of zinc sulfide. Moreover, as Zn compounds are poor Raman scatterers no bands were detected, while the characteristic infrared absorptions of the two pigments are out of the 4000-750 cm^{-1} IR region employed in this study. The presence of titanium white also complicates both SEM-EDS and Raman analyses.

With the exception of the sample collected on the sky, which shows only one pictorial layer, the other cross-sections are made of several overlaid layers. Unfortunately their thickness of about 5-10 µm did not allow a FTIR characterisation for each layer, due to spatial resolution limit.

Blue pigments. Several shades of blue, from dark to light blue, were analysed on all the samples. The elemental composition consisted of Na, Al, Si, S, K, Ca, Ti and Fe (Ca and Ti likely associated to calcium carbonate and titanium white, respectively), and the Raman band at 545 cm^{-1} univocally identifies ultramarine blue (Figure 6.11); this pigment is likely to be artificial due to the round-shape of the crystals [17–19]. In one occasion Co and Sn were found by SEM-EDS, possibly related to cerulean blue. A few grains contained cadmium, most likely cadmium yellow, and others are iron-based, linked to ochres. Weak peaks of Zn and Pb are probably related to zinc white and lead white, respectively. White pigments (titanium white in the anatase form and calcium carbonate) were mixed in each layer in order to achieve the desired hue, but it was not possible to distinguish if they were intentionally added in the paint formulation or present as extenders of other pigments.

Green pigments. Sample nr. 2 contains a final green layer, but no green pigment was identified. Titanium white in the anatase form is the main white pigment, mixed with barium sulfate and calcium carbonate. Moreover, a few red and yellow iron-based grains are likely identified as ochres, and black particles made of Ca and P are possibly associated to bone black. Zn is possibly associated to zinc oxide or zinc sulfide. Interestingly, sample nr. 3 shows a final green layer where Pigment Green 8 (PG8, nitroso green, *Colour Index* 10006) was identified by Raman [34]; the sample was collected on a restored area and the identification of this green layer as an original material or a retouched one was difficult to achieve.

Brown pigments. Raman analysis on the brown colour of the landscape (nr. 4) identified the bands at approximately 1320 and 1600 cm^{-1} related to a black carbon-based pigment. The presence of Fe is likely associated to ochres and Ca and P to bone black. Unfortunately, the layer thickness of 4-8 µm did not allow any FTIR investigation.

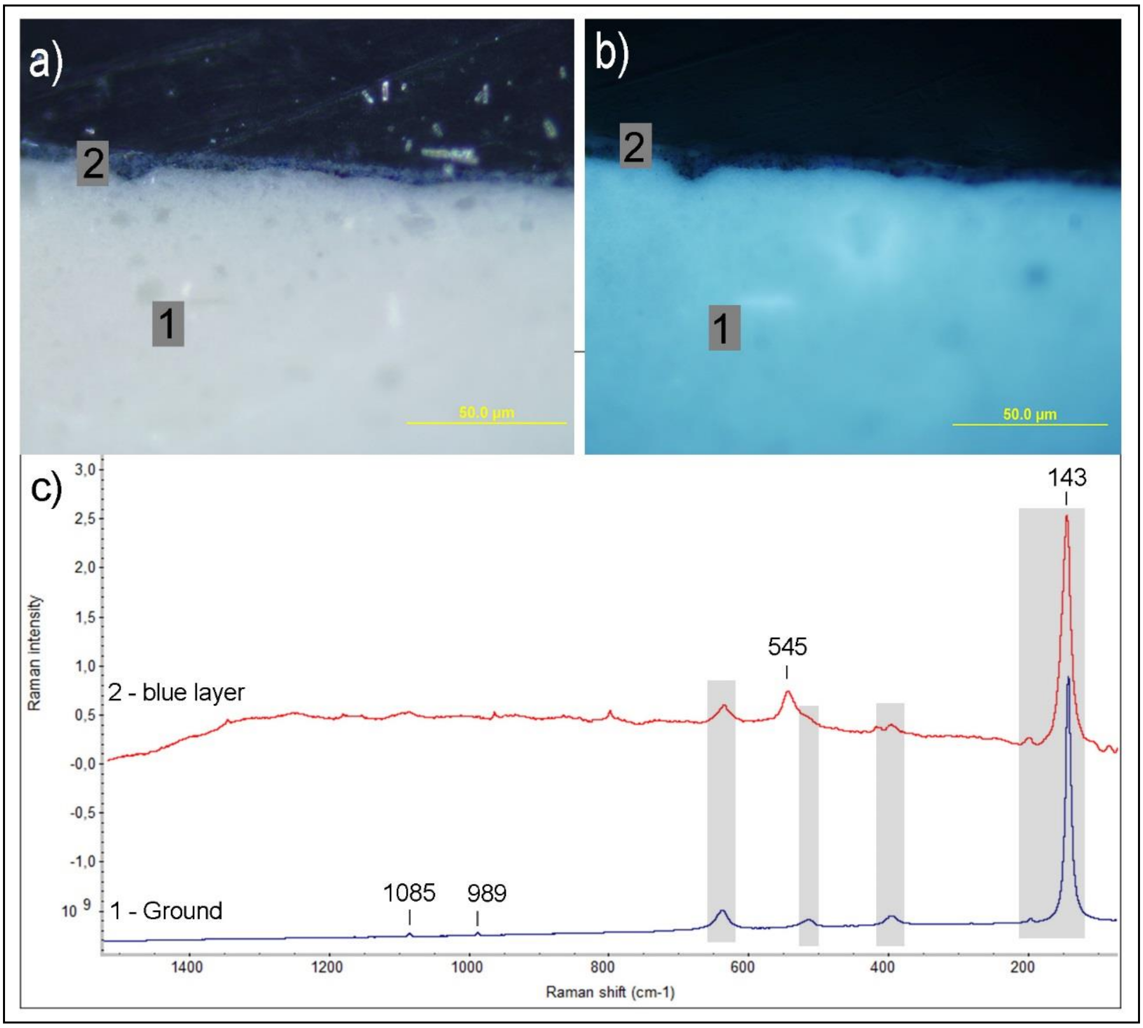

Figure 6.11. a) Cross-section of sample nr. 1, b) under UV; c) Raman spectra showing the presence of titanium white (indicated by the grey squares and the predominant peak at 144 cm^{-1}), barium sulfate (989 cm^{-1}), calcium carbonate (1085 cm^{-1}), ultramarine blue (545 cm^{-1}).

Binder medium. For each sample, FTIR absorptions at approximately 2918, 2850 and 1730 cm^{-1} are related to a drying oil. Weak peaks at 1538 and 1398 cm^{-1} are found in two samples (nr. 2 and nr. 3) in the lower section of the paint layers and identified as zinc carboxylates (possibly zinc stearate and/or palmitate) (Figure 6.12), indicating the beginning of degradation process between the binder and the zinc pigment [35–37].

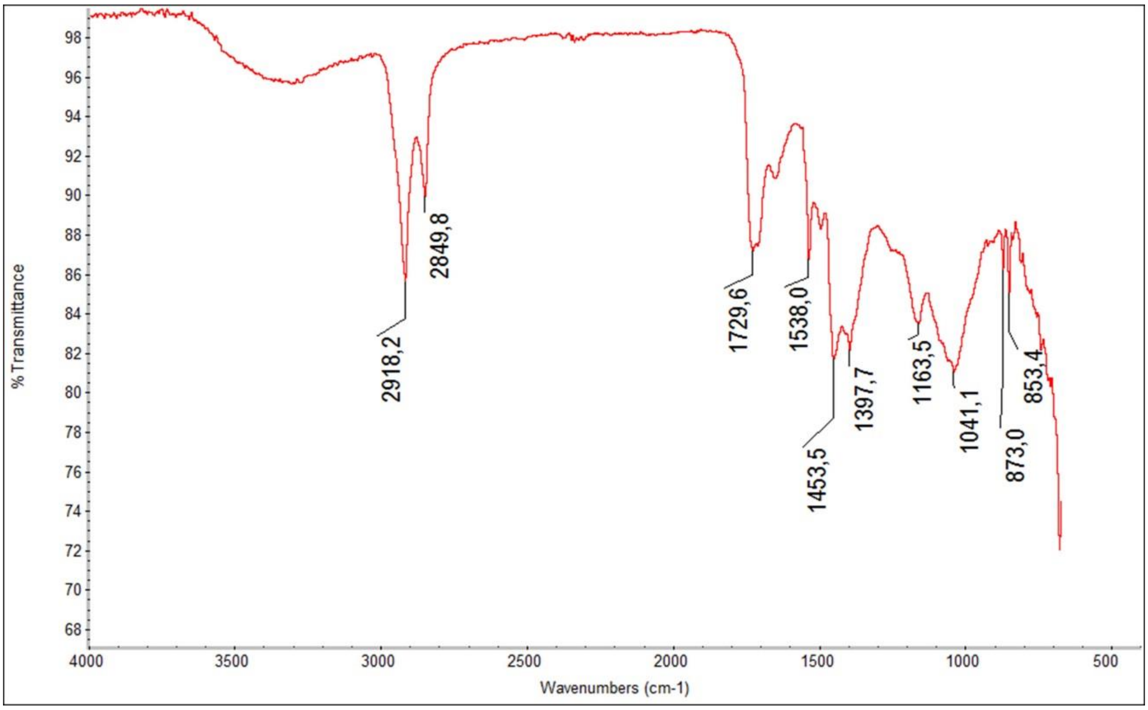

Figure 6.12. FTIR-ATR collected on the blue layer of sample nr.2, showing the presence of zinc carboxylates.

Restoration materials. SEM-EDS analyses of the yellow retouched area on the trees (sample nr. 3) (Figure 6.13) indicate the presence of zinc, which is most likely linked to the use of zinc white due to the intense and characteristic UV fluorescence. Moreover, the presence of iron and cadmium also identified by SEM-EDS are hints for yellow ochres and cadmium yellow. Titanium white (anatase form, as identified by Raman) is the predominant white pigment.

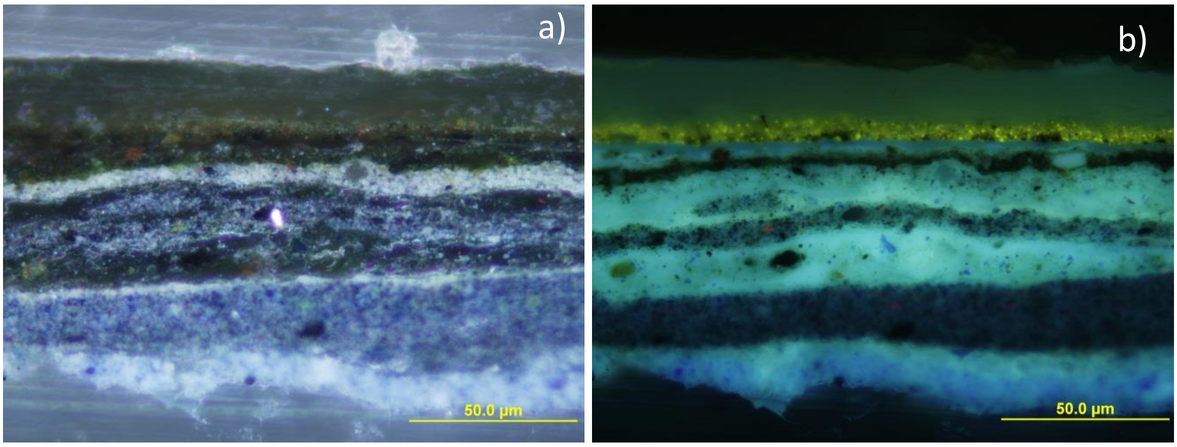

Figure 6.13. Cross section of sample nr. 3, a) visible light, b) under UV.

The thick varnish applied by the restorer as a final layer on the samples is identified as Laropal A81 resin [38] (Figure 6.14). This is a low molecular weight urea-aldehyde resin, developed by BASF (Badische Anilin- und Soda Fabrik) in the 1990s, as substitute for ketone resins, such as Laropal K80, due to their tendency to auto-oxidation [39, 40]. Laropal A81 can be used as a varnish [41] or as a binding medium for retouched paint areas, due to its stability and optical and working properties. Its commercialisation began at the beginning of the 21th century [42, 43].

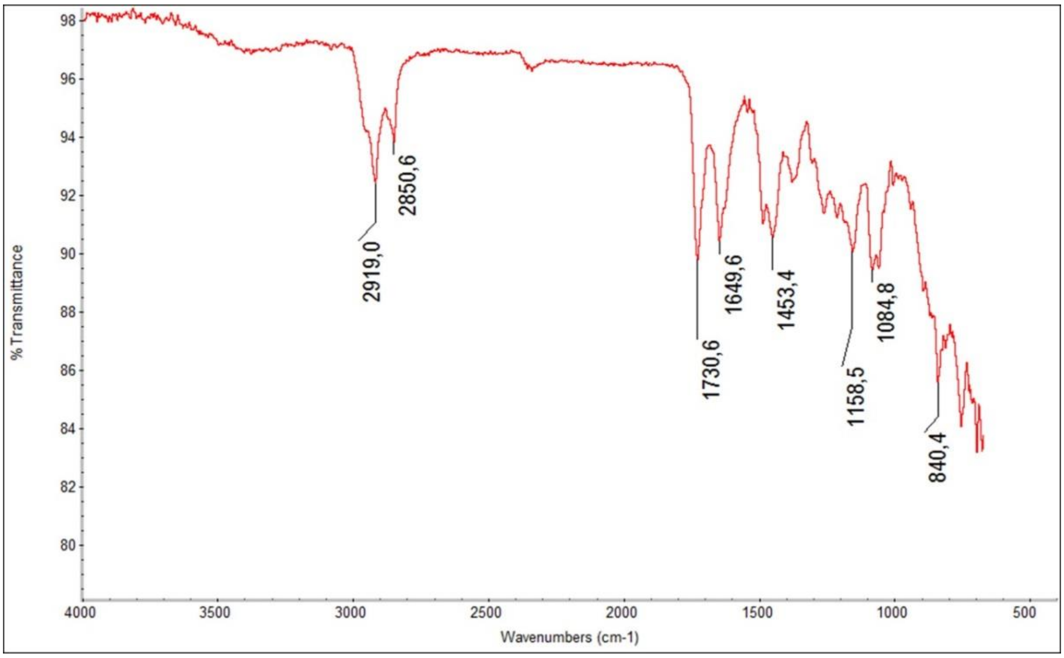

Figure 6.14. FTIR-ATR spectrum collected on the varnish and identified as Laropal A81.

Table 6.3. The results of SEM-EDS, FTIR and Raman microscopy on the colours analysed on the painting.

Colour and sample	**SEM-EDS**	**FTIR (cm^{-1})**	**Raman (cm^{-1})**
White ground (common to all samples)	S, Ba, Ti, Zn	1180, 1107, 983 (barium sulfate) 1650, 1470, 1450 1410, 872, 855 (calcite, aragonite,) 2920, 2850, 1730 (drying oil)	143, 395, 510, 640 (anatase) 989 (barium sulfate) 1085 (calcite)
Blue (samples 1-4)	Na, Al, Si, S, K, Fe Ti, Ca, Zn Cd, Pb, Co, Sn	2925, 2850, 1730 (drying oil) 1650, 1450, 1410, 875, 855 (calcite, aragonite) 1535, 1398 (zinc carboxylates) ~1000 (ultramarine blue)	545 (ultramarine) 140, 390, 515, 635 (anatase) 1085 (calcite)
Green (samples 2 and 3)	Fe, Ca, P, Zn	1175, 1105, 1067 (barium sulfate) 1650, 1470, 1450, 1410, 876 and 852 (calcite, aragonite)	143 (anatase) PG 8 (only on sample 3)
Brown (sample 4)	Fe, Ca, P	-	1320, 1600 (carbon black)

6.2.5 Discussion

The dating of the support material indicates that the tree used for the wooden panel was still growing at the time of Ruyscher's death. The wiggle-matched sequence of radiocarbon dates is therefore the first piece of evidence indicating a fraud. However, the ^{14}C analysis reaches its limit in the question whether it is a simple misattribution or a modern false, therefore material characterisation becomes necessary.

Although the pictorial layers contain traditional pigments, such as lead white and ochres, some anachronism with Ruyscher's life are found. Indeed, ultramarine blue and sporadic grains of cadmium yellow can be identified, both of which were only introduced on the artist market in the first half of the 19th century; cerulean blue was commercialised since the second half of the 19th century [19]. Pigment Green 8, which was identified in the restored areas, was patented in 1885 but only industrially exploited as a pigment material since 1921 [44, 45].

Within the ground layer, zinc and titanium were observed, both of which contradict an attribution to 17th century. Indeed, the use of zinc oxide as pigment began in the late 18th century but become successful in 1834 when introduced as Chinese white [19], while in its sulphide form and in combination with barium sulfate, commonly known as lithopone, was commercialized in 1874 [19]. However the most decisive indication of the painting's date is found in the presence of titanium white in the form of anatase, commercialised in 1919 [9].

Therefore, the material characterisation of the ground and pictorial layers indicates a creation in the 20th century, in particular as of the 1920s due to the presence of titanium white in the anatase form. It may be noticed that PG 8 is also a marker of the 1920s, though it is possibly present in a restored area and therefore this later addition could have been made at any time after the creation of the object.

A timeline combining all the results underlines the discrepancies between the ages of the used support and introduction dates of pictorial materials with Ruyscher's lifetime (Figure 6.15). The incompatibility between the collected data and death of attributed artists is marked by numerous material anachronism. Based on the date of commercialisation of titanium white, the painting was most likely painted at the beginning of the 20th century, which coincides with the rediscovery of Ruyscher art period and the ancient support could indicate a possible fraud aim.

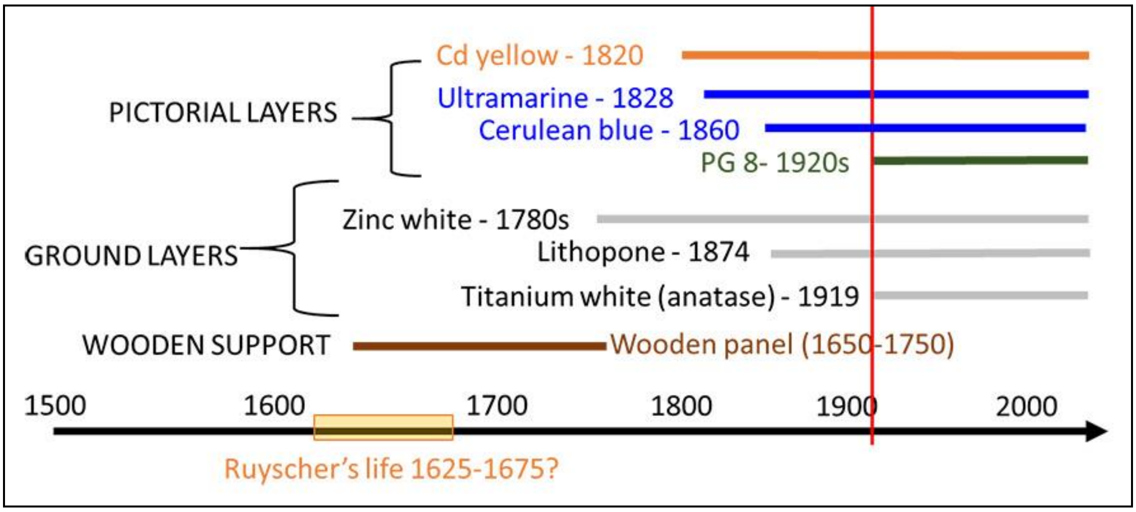

Figure 6.15. Timeline of the overall results: the identified materials with their date of commercialization and the dating found for the panel are inconsistent with Ruyscher's lifetime. The red lines indicate the *terminus post quem*.

6.2.6 Conclusion

The series of techniques applied in the analysis of *Paysage aux roches* attributed to Jan Ruyscher provided decisive arguments for the classification of the object. Radiocarbon dating on the wooden panel identified the chronological range 1650-1750, meaning that the tree was still growing after Ruyscher's death around 1675. Based on the dating of the support material only, the mid-18th century is a definite *terminus post quem* for the production of the painting, which is the first anachronism with the attribution to Ruyscher.

In order to define if it was a misattribution or a forgery, the characterisation of the pictorial layers was carried out. Numerous material anachronisms are found within the pictorial layer, it is however in the ground layer that the most decisive indication of the painting's date is found, indeed the presence of zinc either as zinc white or lithopone and titanium white in the form of anatase contradict a possible attribution to the late 17th century. The presence of anatase in the ground layer of the painting and this uniformly over the panel proves beyond doubt that the execution of the painting could not have executed at an earlier date than 1920. The painting was allegedly painted after 1930s, when Ruyscher's artworks were rediscovered and became noteworthy, or after 1998, when the Bassenge auction house sold a copy of the engraving held at the Rijksmuseum. Even if the signature on the back could be a genuine misattribution, the ancient support is a clear evidence of a fraud intent and therefore the object is classified as a forgery (counterfeited painting).

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Chapter 7

Conclusions

7 Conclusions

This doctoral thesis was designed to propose and evaluate a best practise approach based on scientific techniques that reinforce, with the integration of other fields of expertise, studies for the attribution and authentication of paintings.

As previously stated, generally speaking, authentication is a matter of opinion and attribution is based on assumptions, bias can then affect an examination based only on human expertise; to untangle this general confusion, the use of scientific techniques is beneficial to decrease the degree of uncertainty by evaluating the pieces of evidence.

Given that one single technique is usually enough to disprove authenticity, and this is well-established and documented by literature review, this research investigated methods that help in corroborating authenticity and exploring compatibility with the attribution. In the case of authentic paintings, for instance, a combined set of techniques allow characterisation of the materials and working methods of the artist, contributing to the compilation of technical databases that can help in future studies. On the other hand, analyses can only confirm or refute compatibility with an attribution, while the step further, which is the authentication of the object, can only be taken with an extensive support and integration of other disciplines and, scientifically speaking, by positive matching of the results with a database of materials and techniques and their evolution over the lifetime of an artist. However, despite an accurate and in-depth investigation, the final authentication of the object will always contain a degree of doubt and subjectivity, as the study is related to something that happened in the past and is strictly linked to an artistic process, which therefore cannot be unambiguously confirmed.

As a result of a literature review, a series of well-established and widely applied techniques for the investigation of paintings were identified. The number of combined techniques changes according to the question to be answered and the degree of detailed study that one wants to achieve. For instance, to understand if Munch’s signature was contemporary to the *Bathing women* painting simple UV radiation was used to highlight the retouched areas, one of which contained the writing; on the other hand, to better understand and define the nature of the *Paysage de montagne*, the integration of radiocarbon dating provided additional and fundamental information that allowed the identification of a forgery.

To understand the nature of the object, reconstruct its history and classify it in one of the categories between an original and a forgery, the contextualisation of the results should be favoured. An

integrated approach – which also considers art-historical studies, stylistic knowledge, documentary research, the study of provenance and so on – demonstrates how a reliable and close collaboration among different professionals is an essential aspect for a comprehensive study of a painting.
The best practise proposed in this research provides approaches studying paintings starting from the information initially available on them, making a first evaluation and identifying four categories. Each one is described and explained using case studies, which help in identifying questions, understanding limits and validating the approach. The results of each category are described below.

a) **Authentic paintings**. Collecting data from artworks considered authentic allows to improve or create technical databases on artists' materials and working methods and their technical evolution over time. This is an essential aspect, because it is only by assessing the materials used by an artist and his/her technical evolution that it is possible to create a solid base for future attribution studies of a painting with an uncertain or unknown attribution. It is also an aid when planning a conservation treatment.
The two proposed cases, based on a non-invasive and a micro-destructive approach, allowed the creation of a first technical database of two artists – Isaac Oliver and Gianpietrino. In this way, a proposed date for undated objects was enabled, thus establishing a proper chronology for known artworks, and, in the case of English portrait miniatures, a reconsideration of the attribution of several objects presenting a technique that did not match the one identified for the artist, thus amending and improving the *corpus* of Oliver's artworks. This research will also serve as a basis for future studies on these artists, as until this moment a little published information was available.

b) **Paintings with documentation and distinctive markings.** The evaluation of markings on paintings provides initial information on the object and therefore hint at an attribution. Approaches for the investigation of inscriptions on the back as well as signatures are proposed, as the aim is to assess if the marking is contemporary to the rest of the painting or added at a later time, and then if it is a misattribution or if there is a fraudulent aim. Only a small number of techniques are required for this investigation, as the initial question is in general specific and ideally simple to answer. At a second point, based on the interest of the research or the owner of the artwork, further analyses can be made to fully understand the type of object.

c) **Paintings with an attribution.** As the attribution expresses a degree of uncertainty, several pieces of evidence should be validated to define compatibility with the initial statement. The first and possibly easier step is the assessment of the chronological and/or geographical compatibility,

through non-invasive and, when possible, micro-destructive approaches, to identify a period and possibly a geographical context; the step further will be the proposal of an artist and the evaluation of this hypothesis.
In the more complex case of verification of compatibility with a suggested artist, scientific analyses of the materials combined with research on the said artist work together to assess compatibility. In the case of the *Mon Amour* painting, although the chronological compatibility with the date proposed by a stylistic study was assessed, the lack of published data on Picasso's materials and technique in the specific timeframe did not allow assessment of possible compatibility. This case reinforces the necessity of sharing results to solve attribution issues.

d) **Unknown paintings.** Artworks without any initial available information are considered unknown paintings. Several techniques were combined and applied to exhaustively characterise the materials and identify a chronological period, possibly a geographical area and ideally an artist. The integration with other fields, such as documentary research and stylistic studies, appears fundamental to properly contextualise the data and gain further insights into the artworks' history.
The *Mona Lisa* painting was thoroughly investigated to characterise the visible painting and the earlier composition underneath, allowing the identification of a date range for both artworks. The reason behind the covering of the first painting is still unexplored as documentary investigation was not carried out in this specific study. The case of *Paysage de montagne*, on the other hand, provided a good case study as the integration of materials characterisation and radiocarbon dating allowed thorough characterisation of the object, the combination with comprehensive documentary research on the artist proposed allowed the contextualisation of the results and the reconstruction of the history of the painting.

In conclusion, this research aims to contribute to the field of attribution and authentication of paintings with a first attempt to organise them into categories, providing approaches for the study of artworks and describing case studies that may also help in the investigation of similar objects in the future. The importance of scientific techniques, already desired and encouraged by the 1994 Nara document, is reinforced as an essential part of the best practise.

The current investigation focused on the use of a number of techniques. On this basis, further research will focus on the integration of other analyses, in an attempt to improve protocols and reach an advanced characterisation of materials. For instance, the improvement of non-invasive analyses protocols – including multispectral imaging and mapping XRF – were widely explored in literature, providing helpful results that should be taken into consideration for a more comprehensive best practise. Further results could also be obtained by enlarging the set of case studies, to improve the reliability of the approach and investigate other issues.

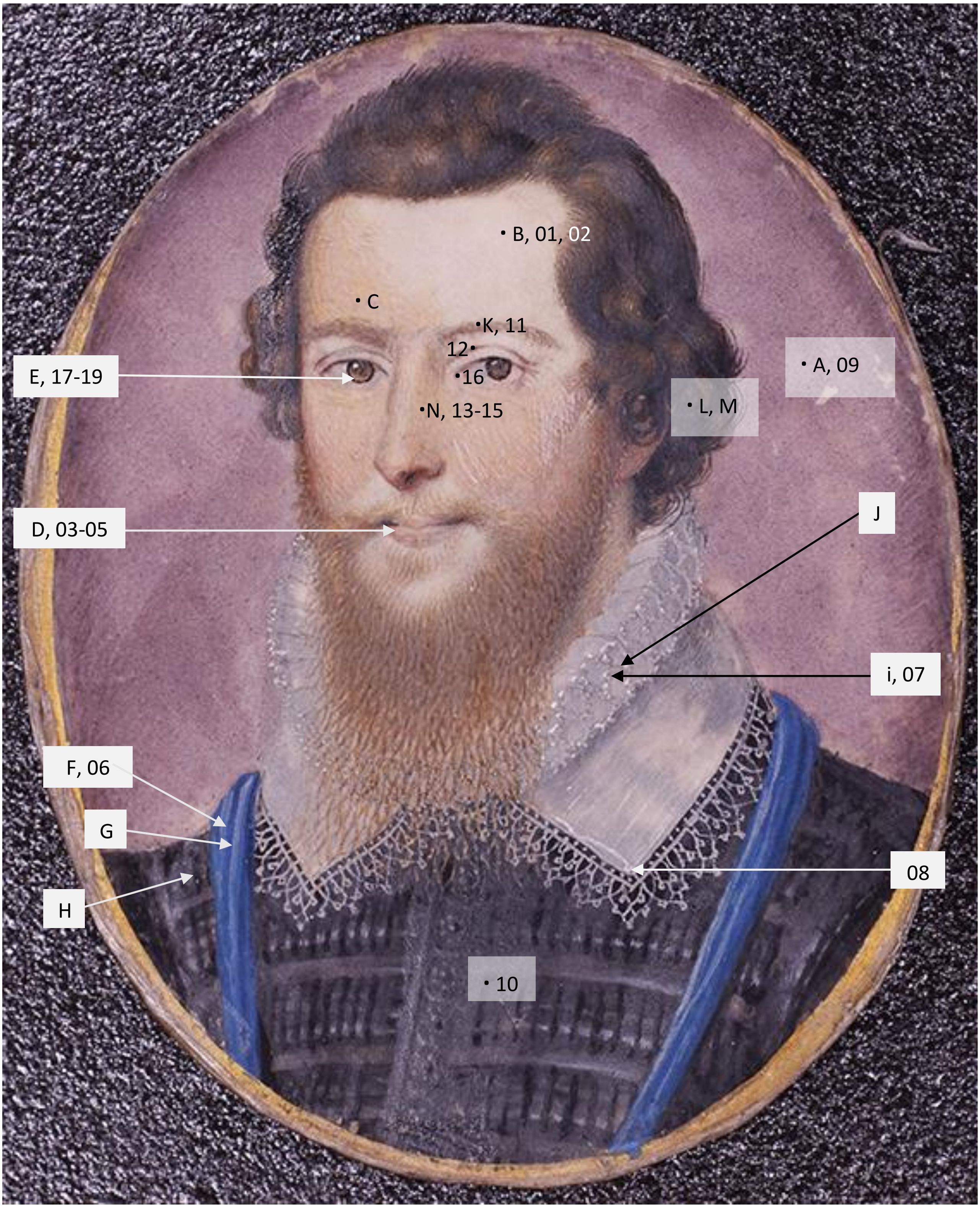
Appendices

Appendix A - Analyses reports of paintings

A.01 - English portrait miniatures

Nr.	Number	Subject	Attribution	Date
1	E.1177-1988	Robert Devereux	Isaac Oliver	1596-1601
2	IS.60-1978	Unknown gentleman + Indian frame	Isaac Oliver	1595
3	P.11-1947	Unknown man (Sir Francis Drake?)	Isaac Oliver	c. 1590
4	P.41-1941	Unknown gentleman	Isaac Oliver	1587-1617
5	P.43-1941	Unknown lady	Isaac Oliver	1595-1600
6	P.129-1910	Portrait of an unknown gentleman	Isaac Oliver	1610
7	P.145-1910	Young girl, aged 4, holding an apple	Isaac Oliver	1590
8	P.146-1910	Young girl, aged 5, holding a carnation	Isaac Oliver	1590
9	630-1882	Sir Philip Sidney	Isaac Oliver	1580-1650
10	E.1178-1988	Unknown man	Nicholas Hilliard	1580-85
11	P.5-1944	Unknown man	Nicholas Hilliard	1597
12	P.8-1945	Unknown lady	Nicholas Hilliard	1590

E.1178-1988 – Robert Devereux



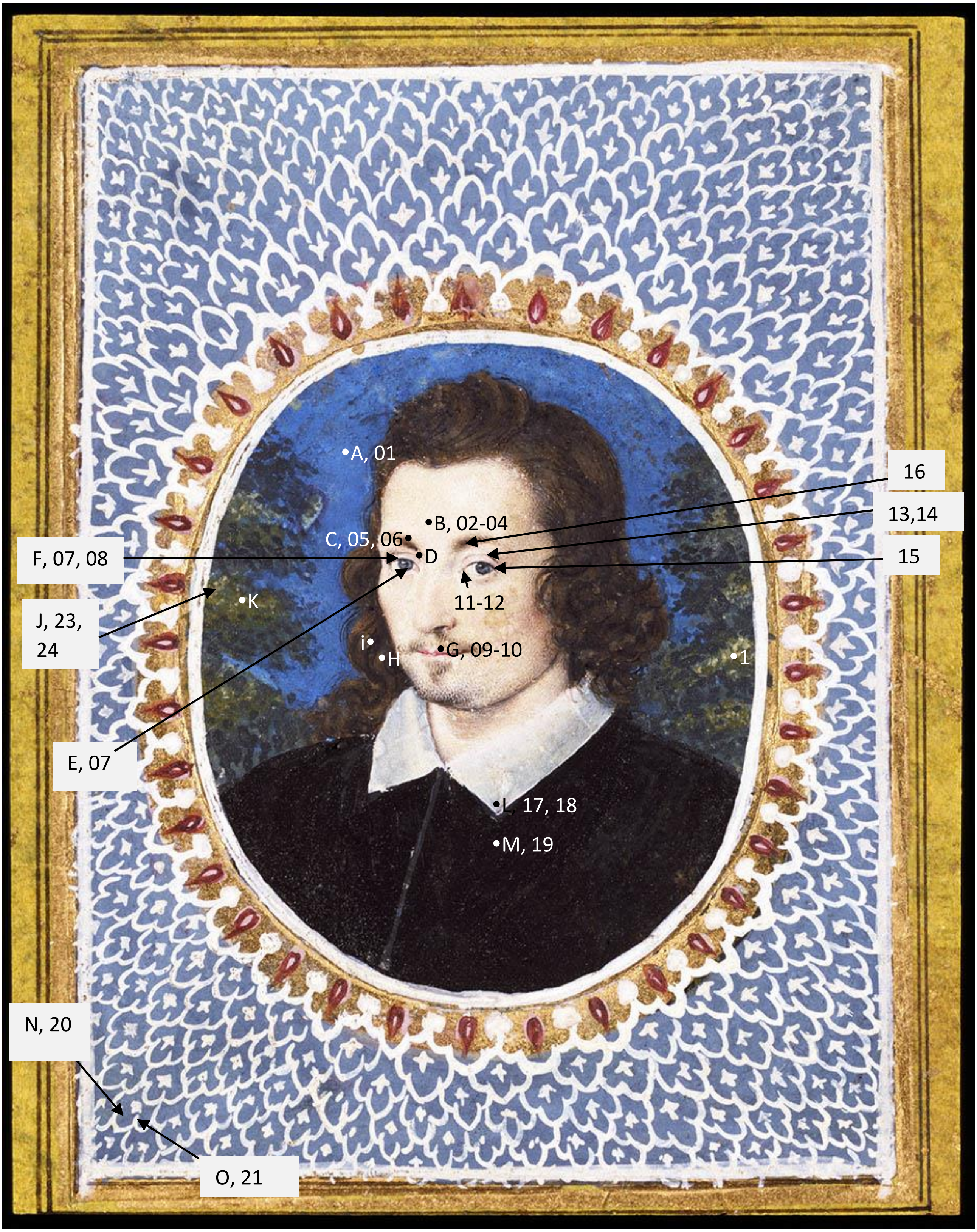
Analysis sites: numbers mark Raman spots, letters indicate XRF spots.

Appendix A.01

Area	Detail	XRF	Raman	Visual examination	Notes
Background (A, 09)	Proper left side	Pb, Fe, Ca, Cu	Red lead	Mixture of dark pink particles, a few pale blue and orange ones	Pink lake and possibly azurite
Forehead (B, C, 01, 02)	Top, proper left side	Pb, Fe, Ca, (Hg)	Lead white, gypsum, vermilion	Pure white matrix with very few finely divided black particles, occasional clusters of crimson red and pale orange particles and a single orange one	The original area under the nose showed also yellow particles. The retouched area on the right side consisted of Ca and Ba.
Nose (N, 13-15)	Middle area	Ca, Ba, Pb, Fe, (Hg), (Cu)	Calcite, hematite	White with red particles, some splodges of yellow lake and occasionally maroon crystals	Retouched area
Eyebrow (K, 11)	Proper left one	Pb, Ca, Fe, Hg, Mn	-	Mixture of black, red and dark yellow particles	Retouched area No spectrum from the yellow particles (yellow ochre?)
Eyelid (12)	Proper left one	-	Carbon black, vermilion	Black and crimson particles	Crimson particles could appear as orange ones
Inner corner (16)	PL eye	-	Vermilion	Mix of red and a few orange particles	Probably retouched
Eyes (E, 17-19)	Proper right one	Pb, Fe, Ca, Hg, Cu, ((Ti))	-	Mixture of yellow, dark red, black and a few red particles	Sclera: lead white
Mouth (D, 03-05)		Pb, Ca, Hg, Fe, (Ba), (Mn)	Vermilion (not saved)	Mixture of red and black particles, a few pale blue ones, and a pale pink lake	Retouched area A medium-rich layer seems to be put on top Likely orange particles underneath
Hair (L, M)	Proper left side, highlight	Pb, Fe, Ca, (Cu), (Hg)	-	-	Mostly retouched
	Proper left side, lowlight	Fe, Pb, Ca, (Hg), (Cu)	-	-	
Doublet (H, 10)	-	Ca, Pb, Fe, Cu, Hg, Mn, P	Carbon black	Very rich in medium with some particles underneath	Possibly bone black
Ribbon (F, G, 06)	Proper right side	Cu, Pb, Fe, Ca	Azurite	Blue matrix scattered with a few orange and brown ones	Middle-grade azurite
Ruff and collar (i, J, 07, 08)	Ruff, proper left side	White Ba, Pb, Ca, Fe	Barium sulfate		
		Grey Pb, (Ca)	-		
	Collar, proper left side	-	Lead white	Top: pure white layer Bottom and middle: grey and off-grey (white matrix with sub-micron red particles)	Top layer: retouched

Appendix A.01

IS.60-1978 – Unknown man in an Indian frame

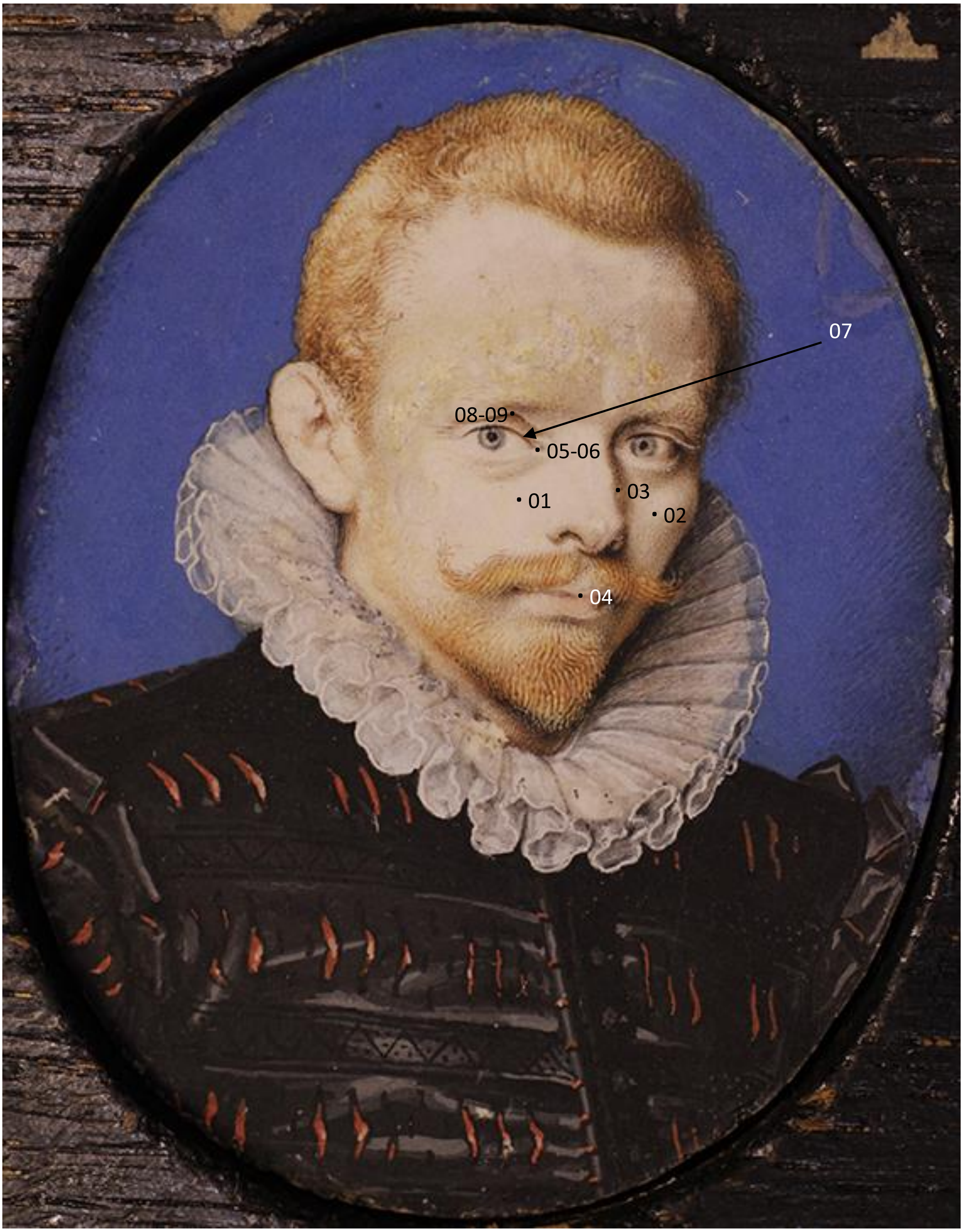


Analysis sites: letters indicate XRF spots, numbers mark Raman spots.

Appendix A.01

	Area	Detail	XRF	Raman	Visual examination	Notes
MINATURE	Blue background (A, 01)	Left side	**Cu**, Pb, Fe, Ca	Azurite	Uniform distribution of blue particles, mixed with some orange-red, brown and yellow ones	
	Flesh tones (B, D, 02-04)	Forehead	**Pb**, Fe, Ca, Cu	Lead white, red lead, vermilion, carbon black	Polished and bright white surface, with a few orange, black and crimson particles	
		Pink area (eyelid) (D)	-	-	Mix of black, orange, a few crimson particles	Red lake/dye, shell gold
	Eyebrows (C, 05, 06, 16)	Left one	**Pb**, Fe, (Cu), Ca	Carbon black, vermilion	Black material with a few dark brown and red particles	
	Iris (E, F, 07, 08)	White glint	**Pb**, Fe, Ca	Lead white	In relief, pure white	
		Blue iris	**Pb**, Fe, Ca	Indigo	Mixture of black and dark blue particles	
	Inner corner (11, 12)	PL eye	-	Red lead, vermilion, indigo		The pink wash probably is due to the indigo
	Eyelash line (15)	PL eye	-	-	Mostly black particles	Likely carbon black
	Eyelid line (13, 14)	PL eye	-	carbon black, indigo	Mostly black	2 lines: the first one has the appearance of the inner corner
	Lips (G, 09, 10)	Upper lip, right side	**Pb**, Fe, Ca	-	Light crimson and black particles	Red lake
		Lower lip	-	Red lead		
	Hair (H, i)	Light area	**Pb**, Au, (Cu), Fe, Ca	-	Mostly dark and maroon particles	Gold particles
		Dark area	**Pb**, (Hg), (Cu), Fe, Ca	-		
	White collar (L, 17, 18)	Right side	**Pb**, Ca, Fe, Cu	Lead white, indigo	A few pale blue particles in a white matrix	No signal for Cu pigments
	Black garment (M, 19)		Ca, **Pb**, Fe, Cu	Carbon black	-	-
	Foliage (J, K, 23, 24)	Green areas	**Cu,** Pb, Fe, Ca	Indigo, hematite	Dull green with some pale-yellow and rare red particles	Mixture of blue and yellow
		Yellow areas		Indigo	-	No signal from the yellow (organic?)
FRAMES	Blue frame (N, O, 20, 21)	Blue background	**Pb**, Fe, **Cu**, Ca	Indigo	Dull blue mixed with white	
		White tracery	**Pb**, Fe, Cu, Ca	Lead white	Pure white	
	Green frame	-	Ca, K, Fe, Pb	Indigo	Yellow dye mixed with a blue pigment	No signal from the organic yellow
	Pink frame	-	Ca, K, Fe, Pb	-	Orange-red dye	No signal, very fluorescent

P.11-1947 – Unknown gentleman

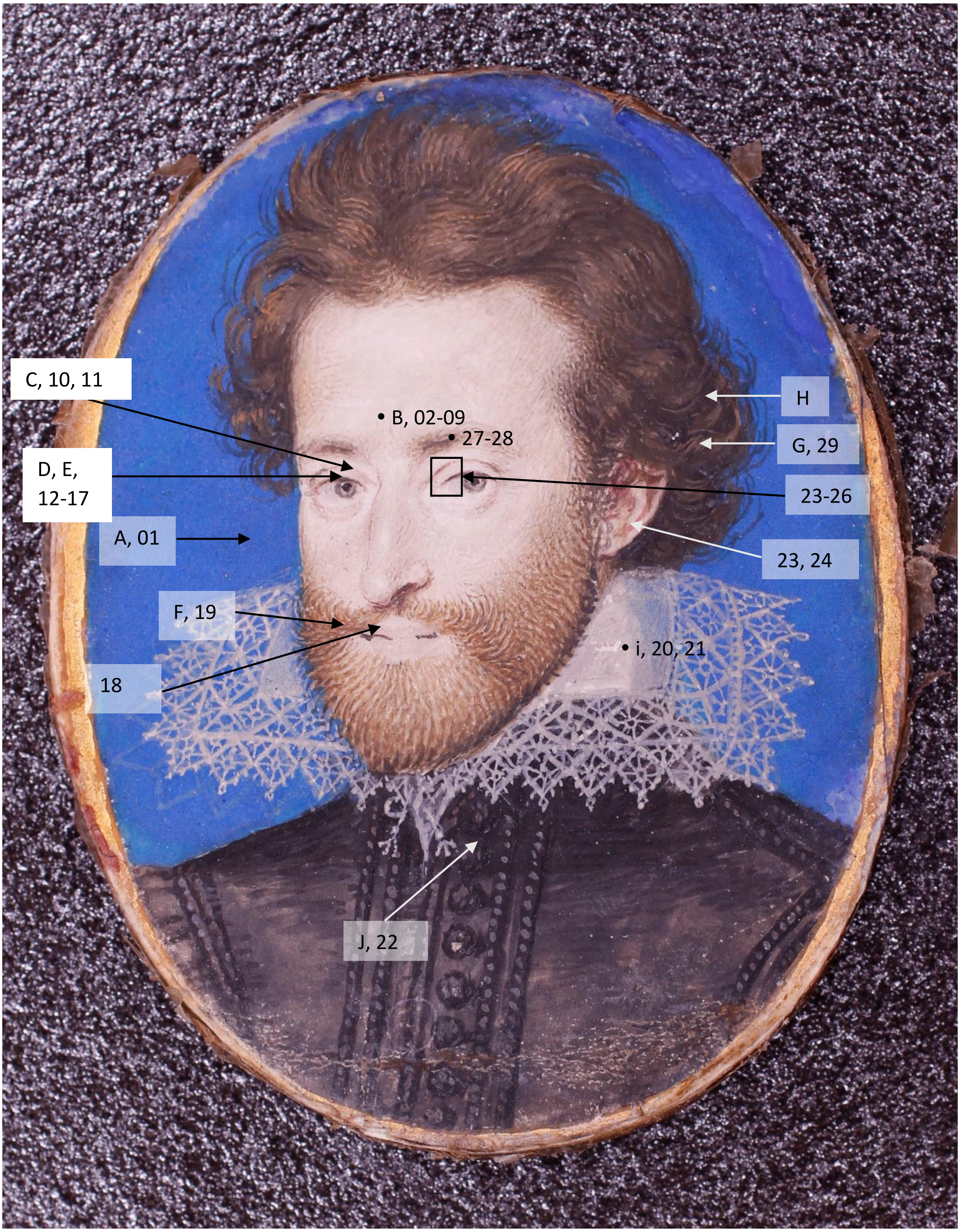


Analysis sites: numbers mark Raman spots.

Appendix A.01

Area	Detail	Raman	Visual examination	Notes
Flesh tones (01-03)	PR cheek (01)	Red lead	White matrix scattered with very sparse red and orange particles	
	PL cheek (02)	Vermilion		
	Nose (shadow) (03)	Vermilion	Mixture of black and crimson red particles	The presence of carbon black is suggested
Eyes (05-09)	Inner corner (05, 06)	Red lead, vermilion, hematite, lead white	Mixture of black, maroon, a few red and yellow particles	The presence of carbon black is also suggested
	Eyelash line (07)	Hematite, carbon black	Mixture of black and maroon particles	Possibly a pink lake was used
	Eyelid line (08, 09)	Vermilion, hematite	Mixture of black and dark red particles with a few maroon ones	The presence of carbon black is also suggested
Mouth (04)		Vermilion	The surface was made of only red particles	No orange particles visible

P.41-1941 – Unknown gentleman

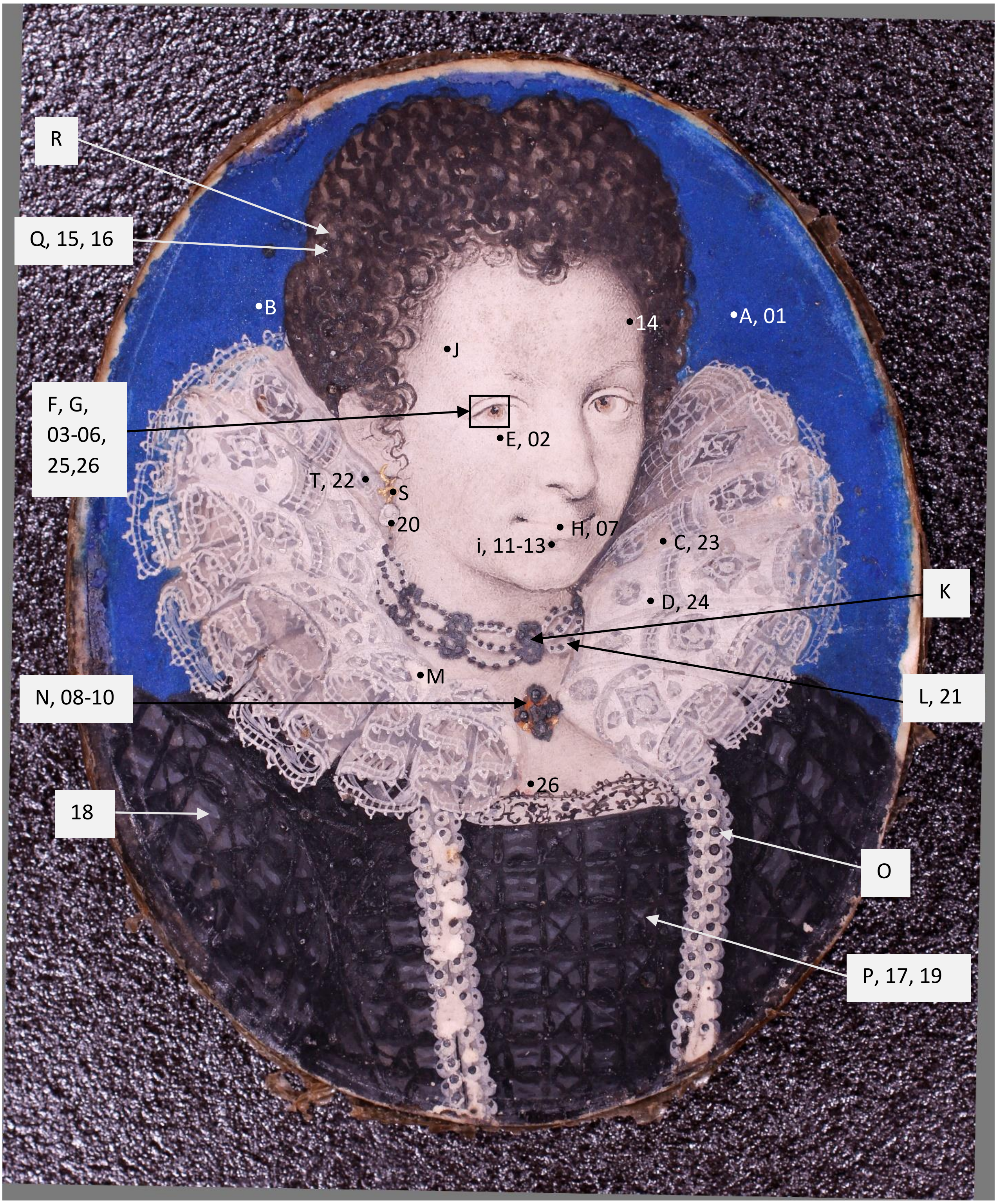


Analysis sites: letters indicate XRF spots, numbers mark Raman spots.

Appendix A.01

Area	**Detail**	**XRF**	**Raman**	**Visual examination**	**Notes**
Blue background (A, 01)	-	**Cu**, (Pb), (Ca), (Fe)	Azurite	-	
Flesh tones (B, 02-09, 23, 24)	Forehead	**Pb**, (Fe), (Ca)	Lead white, hematite, goethite, red lead	White matrix, yellow and black particles, a few red and orange ones	
	Ear (23, 24)	-	Hematite	Finely divided burgundy particles	Dark pink lake/dye
Mouth (18)	-	-	Red lead	Large orange particles on top of a black line	
Eyes' area (C-E, 12-17)	White glint (12)	**Pb**, Fe, Ca	Lead white	In relief, purely white	
	Blue iris (13-17)	**Pb**, Fe, Ca	Azurite, lapis lazuli	Dark blue and pale blue particles	
	Inner corner (23)	-	Red lead	A few orange particles scattered around	
	Eyelid line (10, 11, 26)	**Pb**, Fe, (Ca)	Hematite, carbon black	Finely divided black and dark red particles	
	Eyelash line 24,25	-	Hematite, carbon black	Mixture of maroon and black particles	2 lines: one maroon overlaid by a black one
Eyebrows (27, 28)	Proper left	-	Goethite	Mixture of black and yellow particles	Yellow: needle shape
Hair	Beard (F, 19)	**Pb**, Fe, Ca	Hematite	Yellow "haze" with black, white and burgundy	
	Hair (G, H, 29)	**Pb**, **Fe**, Ca, Cu	Goethite, carbon black	Mixture of black and yellow crystals	Some needle shaped yellow crystals are present
Ruff (i, 20, 21)		**Pb**, Ca	Lead white, azurite	Off-white matrix, finely divided black and some pale blue particles	
Jacket (J, 22)		**P**, **Ca**, **Pb**, Fe, Cu	Carbon black (bone black)	-	

P.43-1941 – Unknown Lady



Analysis sites: letters indicate XRF spots, numbers mark Raman spots.

Appendix A.01

Area	**Detail**	**XRF**	**Raman**	**Visual examination**	**Notes**
Blue background (A, B, 01)	Left and right side	**Cu**, Pb, Ca, Fe, (Ti)	Azurite		
Flesh tones (E, i, J, 02,11-13, 14, 26)	Cheek (under the eye)	**Pb**, Ca, Fe	Lead white	surface appeared flat and white with finely divided black particles.	
	Forehead (lacuna)	Pb, Fe, Ca			
	Forehead (shadow)	-	Vermilion	Several big crimson particles.	
	dark area (under the lips)	**Pb**, Fe, Ca	Carbon black, lapis lazuli, red lead		Lapis only in shadowed area, very few orange, rare vermilion (not saved).
	Cleavage	-	Vermilion	Large and small red particles	
Eyes (F, G, 03-06, 25, 26)	White glint	**Pb**, Fe, Ca	Lead white	In relief, pure lead white.	Looks with indigo (no spectrum obtained)
	Brown iris	**Pb**, Fe, Ca, (Cu)	Hematite, lead white, calcite, carbon black	Particles dispersed in a yellow wash.	No identification on the yellow wash.
	Eyelash line	-	Carbon black	Only black particles	Eyelid line and eyebrows looked the same: no coloured components at all, only black particles.
Lips (H, 07)	Centre	**Pb**, Fe, Ca	Red lead	diluted pink lake, with a few orange particles	Dilute pink lake
Hair (R, Q, 15, 16)	Lowlight	**Pb**, Fe, Ca, Cu	Vermilion, Arsenic-based pigment (in 1 case)	black matrix with some crimson red particles and a few pale blue and orange ones	Azurite and orange iron oxides (not saved)
	Highlight	**Pb**, Fe, Ca, Cu	-		
Ruff (C, D, M, T, 22-24)	Right side	**Pb**, Ca, Fe			
	Lacuna	Pb, Fe, Ca			
	Left side (grey)	**Pb**, Fe, Ca	Lead white, carbon black		
Necklace (K, L, 21)	Pearls	**Ag**, **Pb**, Hg, Fe, Cu			Silver (traces of Cu, Hg, Fe)
	White strip	**Pb**, Fe, Ca			Lead white
Jewel (N, 08-10)	Red area	**Pb**, Fe, Ca	Red lead, goethite	Orange and red crystals mixed with black ones	
Earring (S, 20)	Golden area	**Au**, Pb, Ca, Cu, Fe			
	White area (pearl)	-			
Dress (P, O, 17-19)	Black area	**Pb**, **Ca**, **P**, Cu, Fe	Carbon black, azurite	mostly black with a few blue particles	
	Bluish area	-	Lapis lazuli	mud flat appearance with a greater amount of small blue particles	

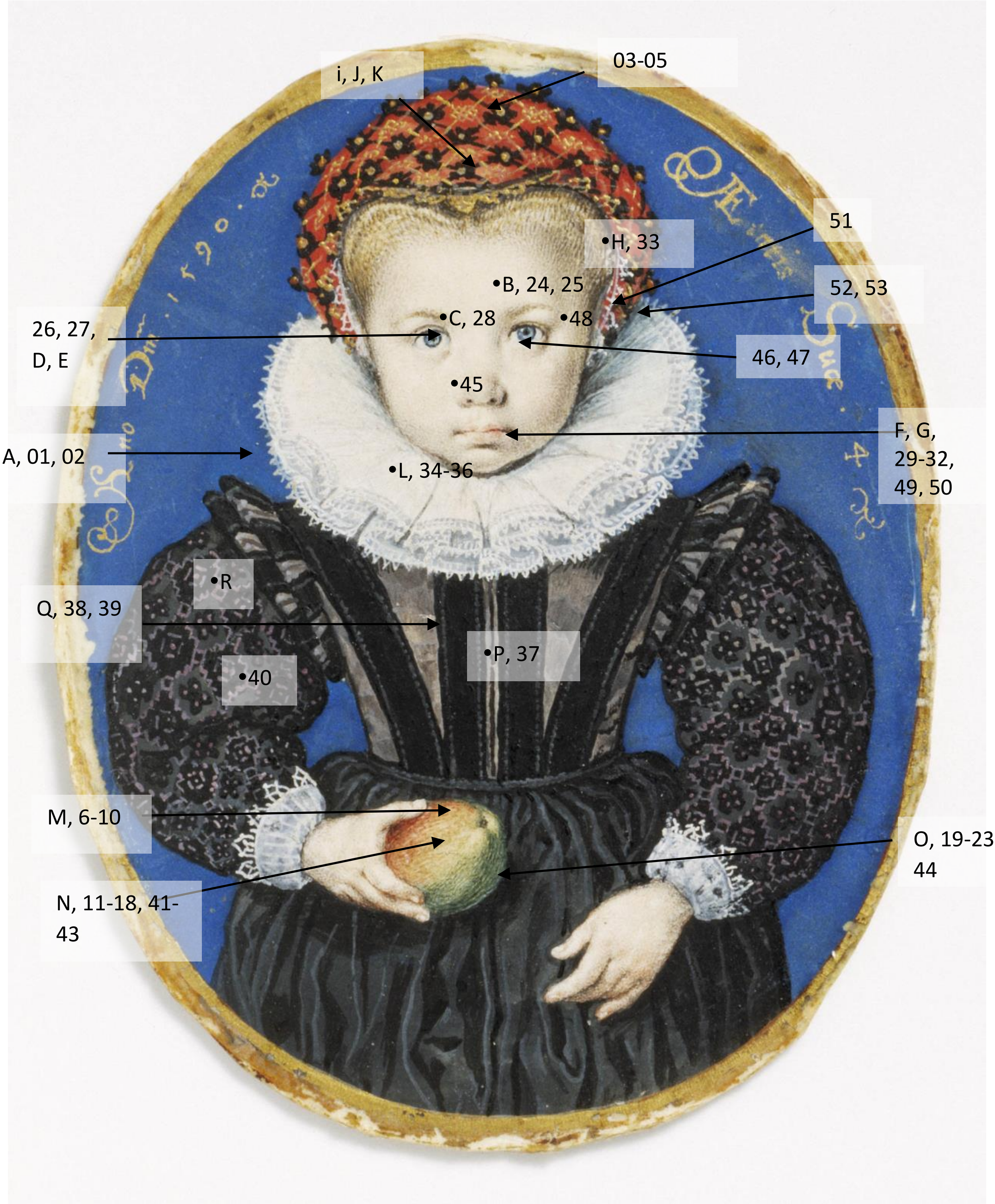
P.129-1910 – Unknown gentleman

Analysis sites: numbers mark Raman spots.

Appendix A.01

Area	Detail	Raman	Visual examination	Notes
Flesh tones (01-05)	White area	Red lead, lead tin yellow type I, goethite, hematite	Mixture of small-sized pale orange particles, boulders and acicular yellow ones and a few red and brown ones	No vermilion seen.
Eyes (08-12)	Inner corner (08)	Red lead	Orange particles	Some light brown lines were drawn on top
	Eyelash line (09-10)	1st line: hematite and carbon black	1st line: maroon and black particles 2nd line on top: mostly black	
	Eyelid line (11)	1st line: goethite and carbon black	1st line: acicular yellow particles and black ones 2nd line: maroon and black particles	2nd line likely made of hematite and carbon black
	Eyebrow (12)	Red lead	Black matrix scattered with a few acicular yellow and occasional orange particles	The presence of carbon black and goethite was assumed
Mouth (06, 07)	PR corner	Hematite, carbon black	Mixture of maroon and black particles	Possibly a dark pink lake was used
	Lower lip	Red lead	Mostly orange particles	

P.145-1910 – Young Lady holding an apple

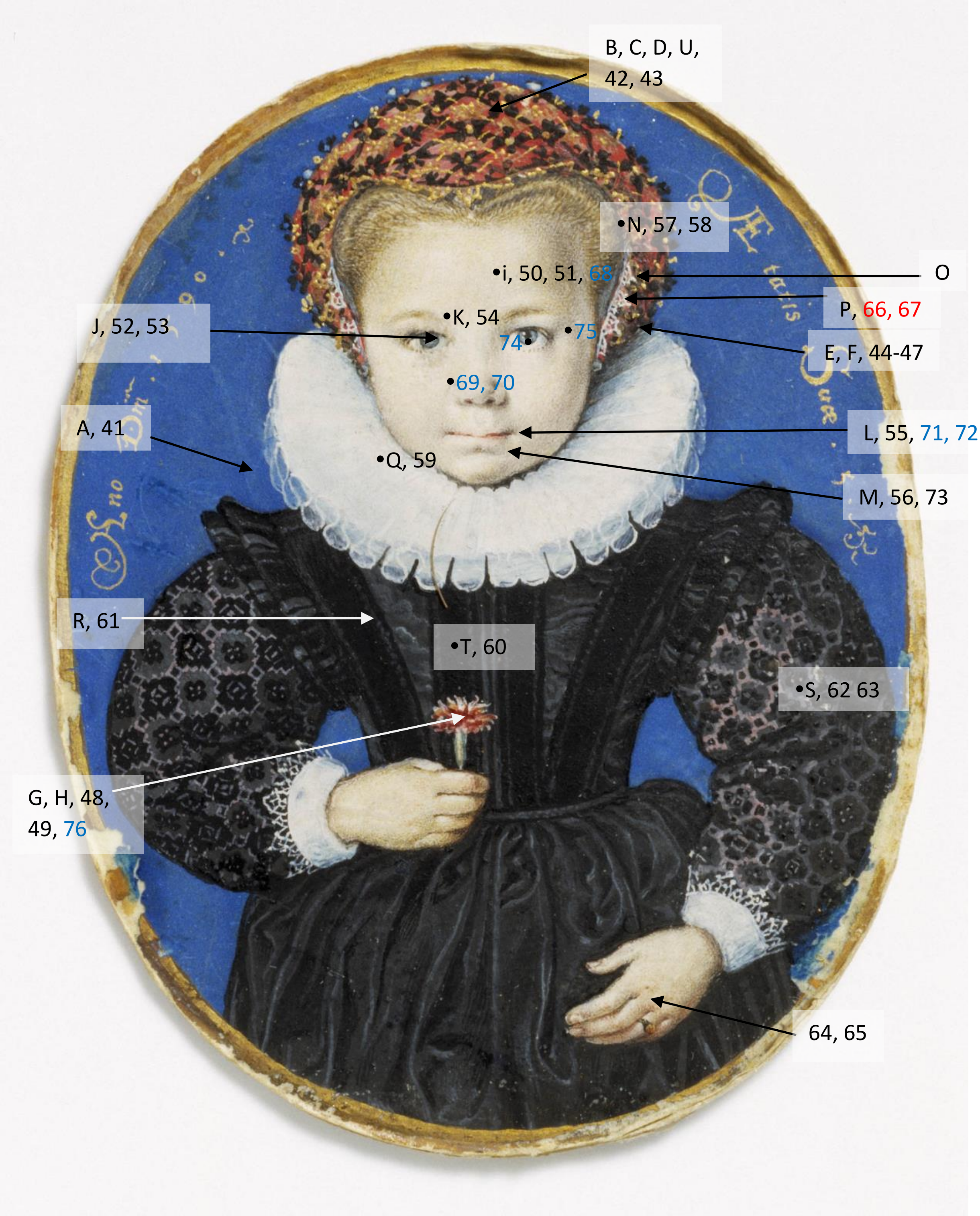


Analysis sites: letters indicate XRF spots, numbers mark Raman spots.

Area	Detail (analysis sites)	XRF	Raman	Visual examination	Notes
Blue background	Left side (A, 01, 02)	**Cu**, Pb, (Ca), Fe	Azurite, (quartz)	A few orange, brown and translucent white particles within the subdued blue matrix.	
Flesh tones	Forehead (B, 24, 25)	**Pb**, Fe, Ca	Lead white, vermilion	White and bright with very fine red and black particles	
	PR cheek (45)		Vermilion, red lead	Red particles and a few orange ones	
	Pink area (under lips) (G)	**Pb**, Fe, Ca	Hematite, indigo	Tiny dark red, maroon particles	
Eyebrow	Left one (C, 28)	**Pb**, Ca, Fe, Cu	-	Some brown particles	The presence of carbon black is assumed, but no spectra were obtained
Eyes	White glint (D)	**Pb**, Fe, Ca	Lead white	In relief, purely white	
	Blue iris (E, 26, 27)	**Pb**, Fe, Ca, (Cu)	Indigo	Dark blue particles mixed with brown ones	
	Inner corner (46, 47)		Indigo, hematite, carbon black	mixture of black and maroon particles	
	Eyelash line (48)		Indigo, hematite, carbon black	black and maroon particles	A second thick and black line was applied only above the iris.
	Eyelid line				Similar to the eyelash A second line made of a brown pigment is applied on top
Lips (F, G, 29-32, 49, 50)	Lower lip, right side	**Pb**, Fe, Ca, Cu, (Hg), (Au)	Vermilion, red lead	Medium-sized orange particles, small-sized red ones and very fine black ones.	Pink dye in the separation line and dark red dye in the corners Carbon black
Hair (H, 33)	Right side	**Pb**, **Fe**, Mn, Ca	Red lead	Stripes made of dark orange, dark brown and black particles	Presence of a light brown dye and gold
Headdress (i-K)	Red areas (i, 03, 04)	**Pb**, Hg, Fe, Ca, (Cu)	-	Red particles	
	White areas (J)	**Pb**, Hg, Fe, Ca, (Cu), K	Vermilion, carbon black	Very finely divided red and black particles	Presence of a pale pink lake K-containing compound
	Gold areas (K)	**Au**, Cu, Fe	-	-	The gold is applied on the white

	Black areas (05)	**-**	Carbon black	Black particles	
	Blue line (51)		Indigo	Finely divided blue particles	
	Orange areas (52, 53)		Pararealgar		
Ruff (L, 33, 34)	Left side	**Pb**, Ca, Fe	Lead white, azurite, indigo	Some blue and very finely divided black particles	Details in relief are pure lead white. Blue particles look like azurite
Dress (P-R, 37-40)	Black stripes (P, 37)	**P**, **Ca**, **Pb**, Fe	Carbon black (bone black)	Black particles	
	Pink stripes (Q, 38, 39)	Ca, **Pb**, Fe, Cu, Co	Massicot, vermilion, indigo	White, beige, dark red, light blue and purplish blue, finely divided black particles.	Blue particles look like azurite and smalt
	Pink details on sleeves (R, 40)	**Pb,** Cu, Fe, Ca, (Hg)	Indigo		Presence of a pink lake
Apple (M-O, 6-10)	Red area (M, 6-10)	**Pb**, **Hg**, Ca, Fe, (Cu), Sn	Lead white, vermilion, lead tin yellow (type I), massicot, carbon black	White, red, medium-sized pale yellow, dull orange and occasional black particles, large dark or black boulders in the shadowed areas	
	Yellow area (N, 11-18, 41-43)	**Pb**, Hg, Ca, Fe, (Cu), Sn	Massicot, lead tin yellow (type I), vermilion, carbon black, indigo	Dull orange, pale yellow, red, blue particles	
	Green area (O, 19-23, 44)	**Pb**, Ca, Fe, Cu, Sn	Carbon black, indigo, azurite, lead tin yellow (type I), massicot	Very finely divided black particles mixed with medium-sized pale yellow, dull orange and blue ones	

P.146-1910 - Young Lady holding a carnation



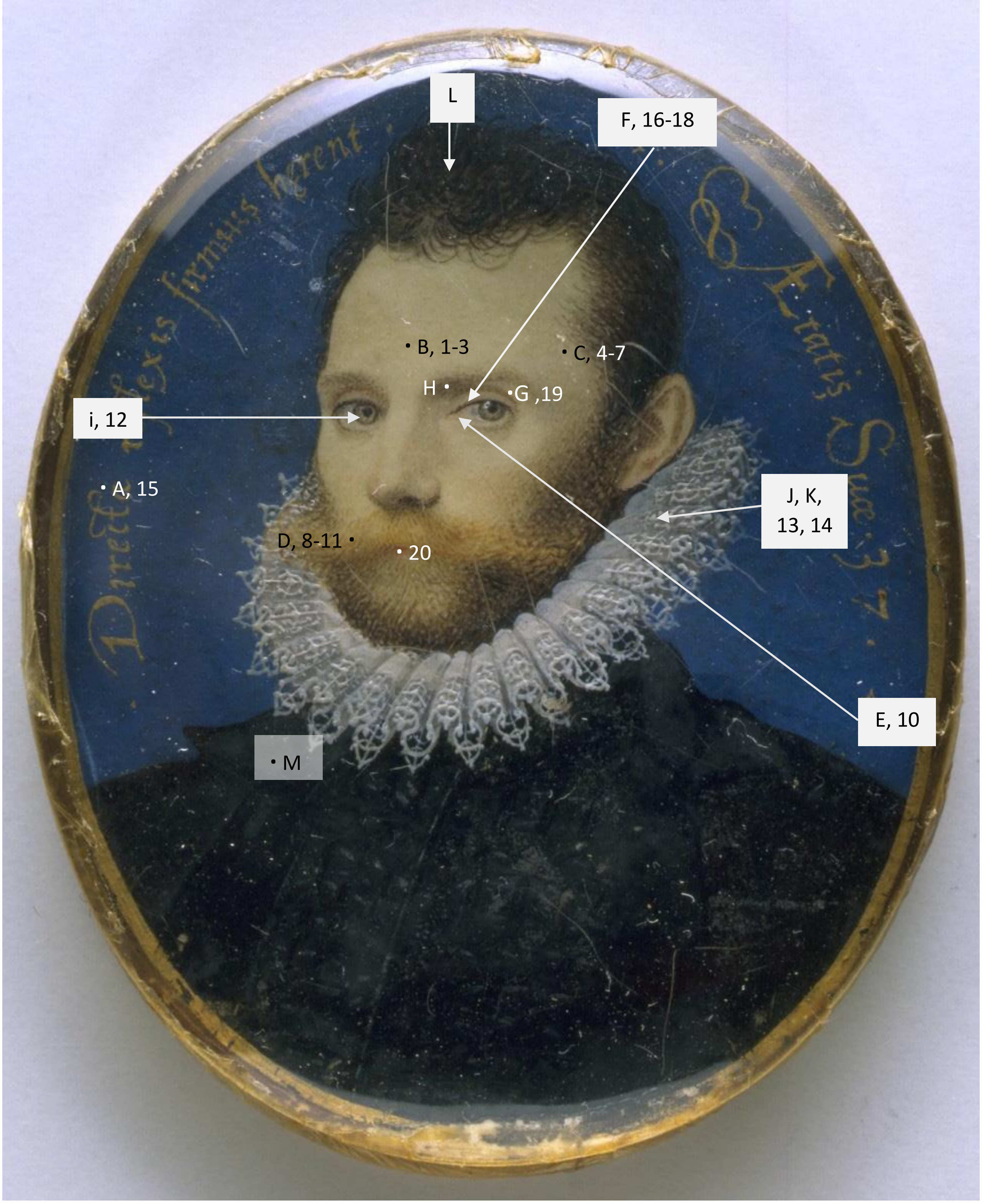
Analysis sites: letters indicate XRF spots, numbers mark Raman spots.

Appendix A.01

Area	Detail	XRF	Raman	Visual examination	Notes
Blue background (A, 41)	Left side	**Cu**, Pb, Ca, Fe	Azurite	Dark blue particles mixed with a few orange, brown and translucent white ones	
Flesh tones (i, M, 50,51,56, 64, 65,)	Forehead (i, 50, 51, 68)	**Pb**, Fe, Ca	Lead white, indigo	White with finely divided black particles and a few orange ones	Some orange particles look like red lead, but no spectrum was collected
	PR cheek (69, 70)		Red lead, pararealgar	Rare orange particles and one dull orange one	two or three azurite-like particles, one crystal that looked like lapis lazuli and two crystals vermilion-looking were present but may be associated to impurities
	Pink area (under lips) (M, 56, 73)	**Pb**, Fe, Ca, (Cu)	Indigo	Finely divided black particles and a few golden ones	
	Hands (64, 65)	-	Vermilion, carbon black	Black, dark brown/orange particles	Presence of a red lake/dye
Eyebrow (K, 54)	Left one	**Pb**, Ca, Fe, Mn	Carbon black	Black and dark brown particles with a few maroon ones	No signal from the dark maroon particles
Eyes (J, 52, 53, 74, 75)	White glint (J, 52)	**Pb**, Fe, Ca	Lead white	In relief, purely white	
	Blue iris (53)	-	Indigo	Grey with only a small portion of blue colour, made of finely divided dark blue particles	
	Eyelash line (74, 75)		Weak signal of indigo in the outer line	Inner line: red lake mixed with black and very rare orange (red lead) and red (vermilion) particles and gold paint Outer line: black, dark brown and a few dull orange particles, and possibly a yellow dye	2 lines: inner area is red and the outer edge is brown
	Eyelid line				Similar to the outer edge of the eyelash line
Lips (L, M, 71, 72)	Lower lip, right side	**Pb**, Fe, Ca, (Cu)	-	Inner corner: black particles scattered in a red matrix Lips: pink lake mixed with black particles; a few azurite-like particles, and gold paint	1 single lapis lazuli particle in the lips. Rare vermilion (possibly as impurities). Red lead belonging to the flesh tones underneath
Hair (N, 57, 58)	Right side	**Pb**, **Fe**, Mn, Ca	Carbon black	Mixture of black, dull yellow and gold particles	No signal from the yellow particles

Headdress (B-D, E, O, U, 42-47, 66, 67	Red areas (B, 42)	**Pb**, **Hg**, Fe, Ca	-	-	Pure vermilion by look
	White areas (D, 44)	**Pb**, Hg, K		-	Less pronounced than in P.145-1910. K-containing compound
	Golden areas (C)	**Au**, Cu, Fe	-	-	
	Black areas (U, 43)	Pb, Hg, Ca	Carbon black	Only black crystals	
	Blue detail (O, P, 66,67)	Pb, Hg, Cu, Fe, Mn, Ca	Azurite	-	
	White lace (E, F, 45-47)	**Pb**, Hg, Cu, Fe, Mn, Ca	Lead white	-	Pararealgar found in areas without lace, gold or black
Ruff (Q, 59)	Left side	**Pb**	Lead white, indigo	White with some finely divided black and occasional pale blue particles	
Dress (R-T, 60-63)	Black stripes (T)	**P**, **Ca**, **Pb**, Fe, Hg, Cu	Carbon black (bone black)	-	
	Pink stripes (R, 60, 61)	**Pb**, Ca, Fe, Cu	Carbon black	-	
	Pink details on sleeves (S, 62, 63)	**Pb,** Cu, Fe, Ca	Vermilion	Medium-sized red, orange, black and a few gold particles	Presence of a pink lake/dye
Flower (G, H, 48, 49, 76)	Orange area (G, 76, 48)	**Pb**, Hg**,** Ca, Fe, Cu	Red lead	Mostly made of orange crystals	White highlights are very fluorescent and show a weak band of lead white
	Crimson area (H, 49)	**Pb**, Hg**,** Ca, Fe, Cu	-	Some medium-sized black particles scattered in a red matrix	Presence of a red lake/dye

E. 1178-1988 – Unknown man



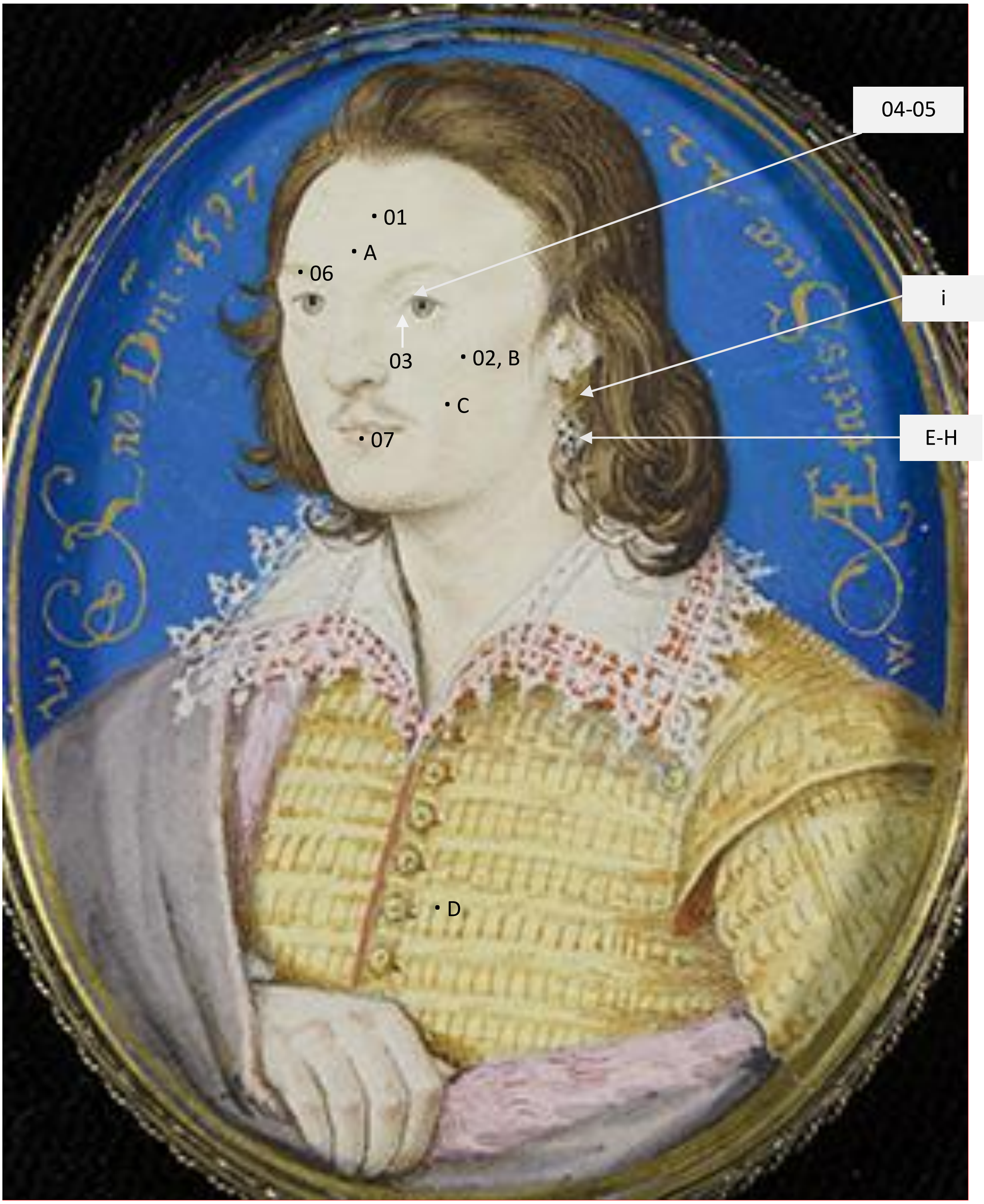
Analysis sites: numbers mark Raman spots, letters indicate XRF spots.

Appendix A.01

Area	Detail	XRF	Raman	Visual examination	Notes
Background (A, 15)	Proper right side	Cu	Azurite	Blue crystals	The mineral impurities of azurite are also visible
Flesh tones (B, C, 1-7)	Forehead (A, 1-3)	Pb, Ca, Fe, (Mn), (Hg)	Vermilion, red lead, hematite, (disordered) pararealgar	White surface scattered with crimson red, dark orange, maroon and dull orange particles	Pararealgar was found only in one case
	Temple (bluer area) (B, 4-7)	Pb, Ca, Fe, (Mn)	Carbon black, pararealgar	Dark brown, maroon and bright yellow particles	Hematite (maroon particles, but no spectra collected)
Moustache (D, 8-11)	Proper right area	Pb, Fe, Ca, (Hg), (As), (Cu), (Mn)	Red lead, hematite, pararealgar, vermilion	Mixture of finely divided yellow particles and orange, bright warm yellow and maroon ones; a few crimson red crystals as well	
Mouth (20)	Central area	-	-	Particles that looked like vermilion mixed with black ones	Probably a mixture of vermilion, carbon black and a pink lake
Eyes (F- i, 12, 16-19)	Inner corner	Pb, Hg, Ca, Fe	Vermilion	Crimson red particles	
	Eyelash (F, 16-18)	Pb, Fe, Ca, (Cu)	Vermilion, hematite(?), carbon black	First discontinued line, made of finely divided red particles. Second dark brown line applied on top: black particles dispersed in a medium-rich layer	
	Eyelid (G, 19)	Pb, Fe, Ca	-	Finely divided vermilion-like particles mixed with black and brown	The second line on top appears brown in comparison to the eyelash line (which is black)
	Eyebrow (H)	Pb, Fe, Ca			
	Iris, proper right one (i, 12)	Pb, Fe, Ca	Indigo	Dark brown particles mixed with a few black and dark blue ones	Possibly carbon black
Hair (L)	Highlight	Pb, Ca, Fe, (Mn), (Cu)			
Ruff (J, K, 13, 14)	Three-dimensional detail	Pb	Lead white	White matrix scattered with a few black and sub-micron red particles	Three-dimensional details
	Off-white background	Pb	Lead white, carbon black	Mixture of finely divided black and white particles	
Doublet (M)	Proper right side	Pb, Ca, P, Fe, (Mn), (Cu)			Possibly bone black

Appendix A.01

P.5-1944 – Unknown man



Analysis sites: numbers mark Raman spots, letters indicate XRF spots.

Appendix A.01

Area	Detail	XRF	Raman	Visual examination	Notes
Flesh tones (A-C, 01, 02)	Forehead			White matrix scattered with a few orange and pale yellow particles	Red lead and lead tin yellow (identified in 2011)
	PL cheek		Hematite	White matrix scattered with a few orange and pale yellow particles and a few dark red ones	
Mouth (07)				Mostly vermilion	Sporadically red lead (from the flesh tones underneath?)
Eyes (03-06)	Inner corner (03)			Pale pink dye	
	Eyelash line (04)			Mixture of black and brown particles	
	Eyelid line (05)			Diluted mixture of black and brown particles	
	Eyebrow (06)			Mixture of black, brown and dark yellow particles	
Doublet (D)	Yellow area	Pb, Sn, Ca, Fe			
Earring (E-H, i)	Silver area	Ag, Pb, Hg, Ca, Cu			
	White and grey areas	Pb, Cu			
	Gold area	Au, Pb, Cu, Fe			

P.8-1945 – Unknown Lady

Analysis sites: numbers mark Raman spots, letters indicate XRF spots.

Appendix A.01

Area	Detail	XRF	Raman	Visual examination	Notes
Background (33)			Azurite	Pale blue particles and the usual impurities of black, brown and orange particles	
Flesh tones (11-13)			Red lead, azurite, goethite	Mixture of white, black, blue, orange particles (orange and dull orange)	Yellow dye
Mouth (14, 15)			Red lead	Mixture of red lead, lead white, pink dye and carbon black	Gold paint was also present
Eyes (H, 16-20)	Iris (H, 20)			Mixture of brown and black particles	
	Inner corner (16)		Red lead	Orange particles mixed with black ones	
	Eyelash line (17)		Carbon black	Outer side: mixture of black and brown particles Inner side: indigo or very finely divided carbon black	2nd black line applied on top
	Eyelid line (18)			mixture of white and finely divided black or blue particles	It looked like carbon/soot
	Eyebrow (19)			Mixture of black and brown	
Hair (i, J)		Pb, Fe, Ca, (Mn)			Higher proportion of iron in the highlight (possible presence of yellow ochre)
Dress (A-C, 26-32, 44)	Green details (26-29)	Cu, Pb, Ca, Fe	Azurite, indigo, lead white and calcite	Mixture of blue and bright yellow particles	Raman spectrum of a bright yellow crystal not identified
	Orange lace (30,31)		Pararealgar (intermediate phase)	Dark orange particles	
	Blue flower (32)		Azurite	Pale blue crystals	
	Pink flower (44)			Mixture of red-pink dye and red lead	
Lace (45-47)	Grey		Lead white, carbon black, azurite	Mixture of finely divided white and medium-sized black particles, with a few large blue ones	
	White		Lead white, indigo	Finely divided white and a few dark particles	
	White, in relief		Lead white	Pure white	In relief
Necklace (34-37)			Main body: lead white, indigo Thick white: lead	Main body: pure white with a bit of black Thick layer: white and	The silver glint was applied on the thick white layer

			white, carbon black Shadow: lead white, carbon black, indigo	finely divided black Shadow: mixture of white, black and dark brown particles, with perhaps a few of tiny red-orange ones	
Neck pendant (D, E, 21-25)	Dark orange area	Pb, Fe, As, Sn, Ca	Pararealgar (intermediate phase) Lead tin yellow type I	Mixture of dark orange and bright yellow particles and rare dark red ones (hematite?)	
	Pale orange area	Pb, Fe, As, Sn, Ca	Lead tin yellow type I Pararealgar (intermediate phase) Red lead	Mixture of pale yellow and dull orange particles and a few bright orange ones	
Tiara (F, G, 38-43)	Dark orange	Cu, Pb, Fe, K, As	Red lead Pararealgar (intermediate phase) Lead tin yellow type I Massicot (1 particle)	mixture of pale yellow, warm yellow, bright orange and light brown and dark orange particles	The dark orange crystals gave no Raman spectrum (iron oxide?)
	Yellow	Cu, Pb, Fe, Sn	Lead tin yellow type I	Uniform pale yellow pigment	

A.02 - Bathing Women

Introduction

Bathing women (Figure A02.01), bearing the signature “Munch” at the bottom right side, depicts three naked women at the poolside. This theme is a permanent feature in the artist’s artworks since 1899, with figures painted individually or as a group of different ages, gender and ethnics, both in an outdoor or indoor environment [1]. A stylistic study on the painting correlated the style with the late period of the artist, who died in 1944.

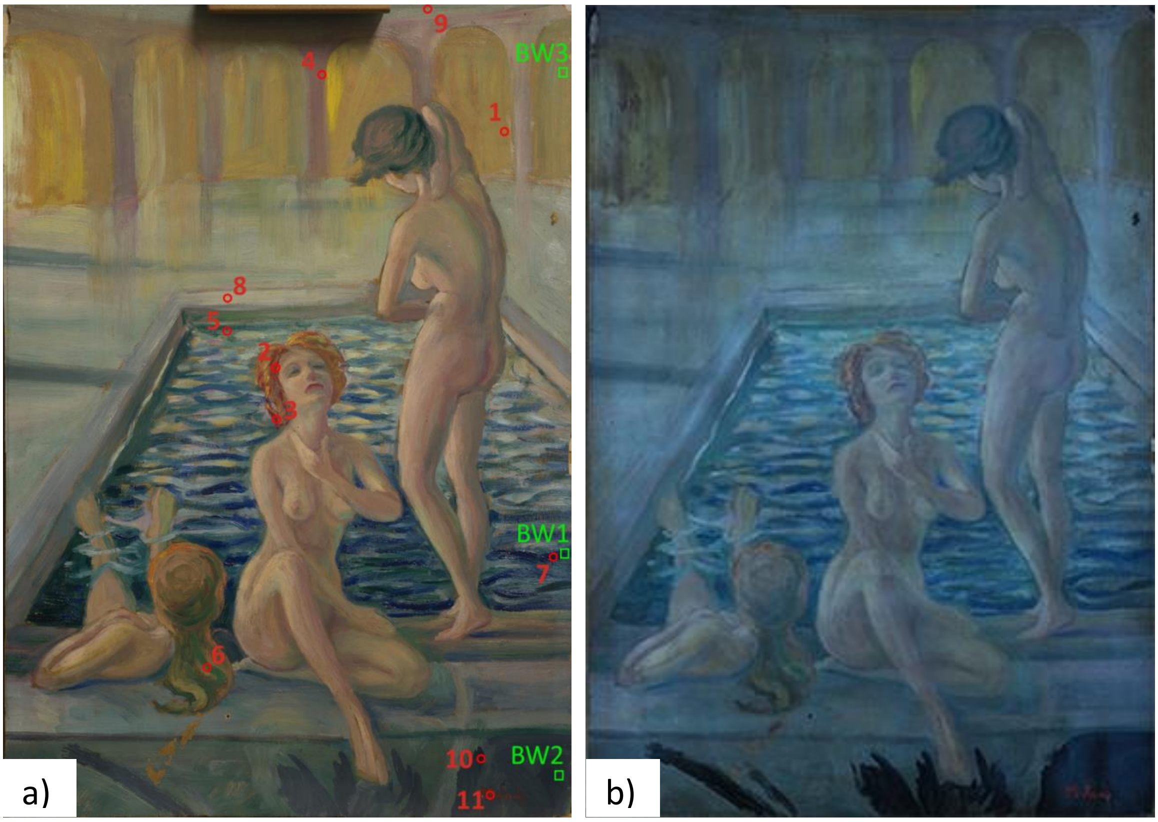


Figure A02.01. a) *Bathing Women*, E. Munch (attributed to), 59x41 cm, date unknown, oil on cardboard. The red circles indicate the XRF analyses spots, the green squares are related to the sampled areas for the cross-sections investigations; b) UV fluorescence.

Results and discussion

Non-invasive imaging analyses hinted at some characteristics useful for further investigations. UV fluorescence (Figure A02.01b), for instance, showed a different response in the area near the signature, at the bottom right of the painting, suggesting different materials in comparison to other areas. The drawing was investigated with IR reflectography (Figure A02.02): a few adjustments in the figures’ outlines (i.e. changes in the arms’ position) and in the lines of the background structure are present. These features are associated to a creative process, therefore the painting is probably not a copy made from an original.

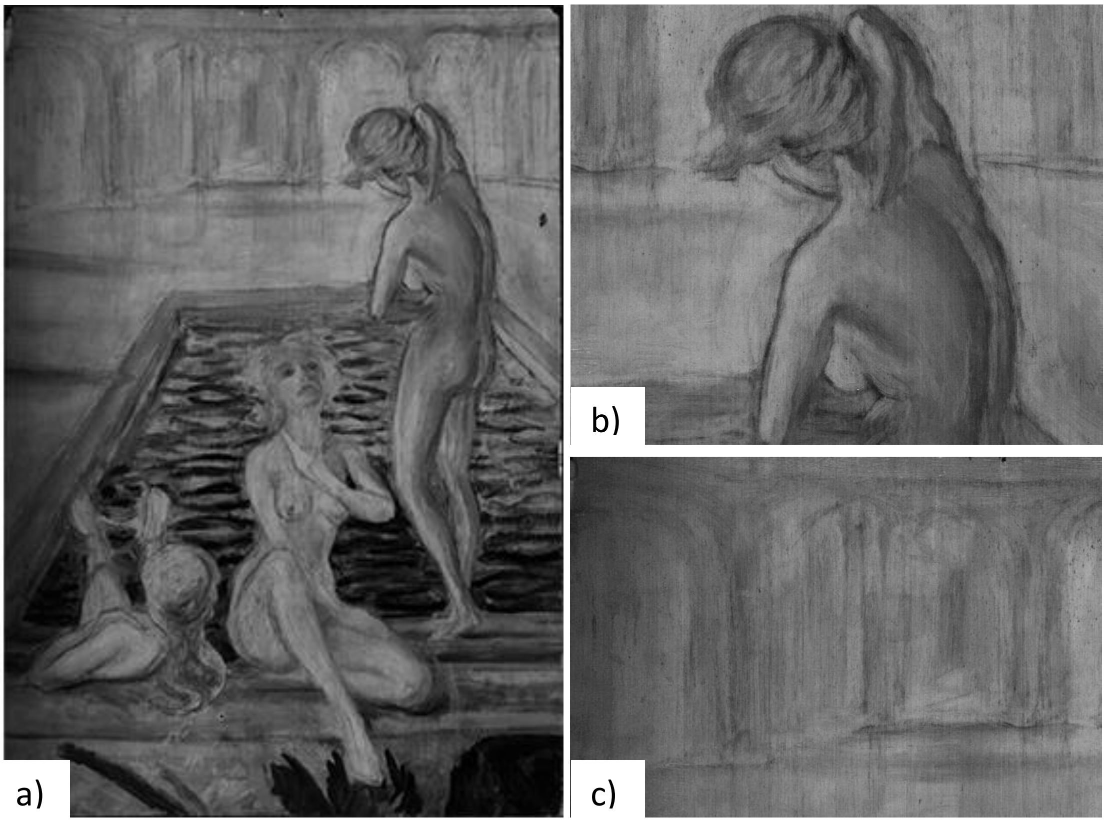


Figure A02.02. a) IR reflectography of *Bathing Women* and b-c) magnification of some details.

By means of XRF, the possible palette of the artist is summarised in Table A02.01. Zinc was the predominant element identified in all the spectra, suggesting the presence of zinc white, although lithopone cannot be excluded. The same elements were identified in several areas of different colour, hence the necessity for sampling. Following these results, three samples were chosen and collected. The possible identification of blue pigments was unresolved by XRF: the presence of Prussian blue could be suggested, but a mixture with other blue pigments could be present as well. Given the interest on the investigation of the signature, two blue samples were collected: one from the water area and another from the area near the signature, characterised by a different UV response. The last sample was taken from a yellow area from the background to identify the mixtures of yellow pigments, after the choice to preserve the flesh tones. The green areas were characterised with a slightly higher presence of chromium, possibly associated to chrome oxides, and the red/orange ones were probably made of vermilion and likely organic colourants, therefore no samples were taken from these areas.

Table A02.01. The spots investigated by XRF on *Bathing Women* are described by the colour of the area investigated and indicated in Figure A02.01. A possible pigment identification is suggested.

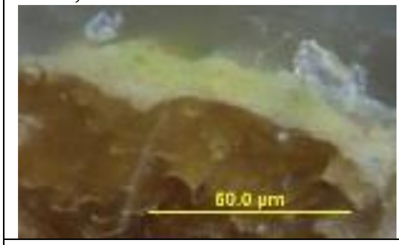
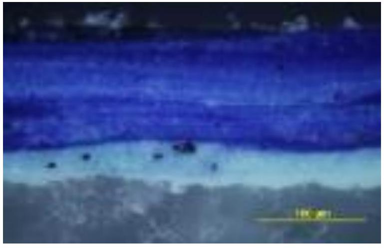
N	**Colour and area**	**Elements identified**	**Possible pigment interpretation**
1	Yellow, background	Ca, Ba, Cr, Fe, Zn, Cd, Hg	Zinc white, lithopone?, Fe oxides, barium sulfate, chrome oxides, cadmium yellow, vermilion, calcium carbonate and/or calcium sulfate
2	Orange, hair	Ca, Ba, Cr, Fe, Zn, Cd, Hg	Zinc white, lithopone?, barium sulfate, vermilion, chrome oxides, Fe oxides, Cd yellow, calcium carbonate and/or calcium sulfate
3	Red hair	Ca, Ba, Cr, Fe, Zn, Cd, Hg	Zinc white, lithopone?, barium sulfate, vermilion, chrome oxides, Fe oxides, Cd yellow, calcium carbonate and/or calcium sulfate
4	Pink, background	Ca, Ba, Cr, Fe, Zn, Cd, Hg	Zinc white, lithopone?, barium sulfate, vermilion, chrome oxides, Fe oxides, Cd yellow, calcium carbonate and/or calcium sulfate
5	Green, water	Ca, Ba, Cr, Fe, Zn, Cd, Hg	Zinc white, lithopone?, barium sulfate, chrome oxides, Fe oxides, Cd yellow, calcium carbonate and/or calcium sulfate
6	Green, hair	Ca, Ba, Cr, Fe, Zn, Cd, Hg	Zinc white, lithopone?, barium sulfate, chrome oxides and/or chrome oxides, vermilion, Fe oxides, calcium carbonate and/or calcium sulfate, Cd yellow
7	Blue, water	Ca, Ba, Cr, Fe, Zn	Zinc white, lithopone?, barium sulfate, Fe oxides and/or Prussian blue, chrome oxides, calcium carbonate and/or calcium sulfate
8	White, edge	Ca, Ba, Cr, Fe, Zn	Zinc white, lithopone?, barium sulfate, Fe oxides, chrome oxides, calcium carbonate and/or calcium sulfate
9	Grey, background	Ca, Ba, Cr, Fe, Zn	Zinc white, lithopone?, barium sulfate, Fe oxides, chrome oxides, calcium carbonate and/or calcium sulfate, carbon black(?)
10	Blue, near the signature	P, Ca, Ti, Cr, Fe, Zn, Hg	Zinc white, calcium carbonate and/or calcium sulfate, Fe oxides and/or Prussian blue, bone black, chrome oxides, titanium white, vermilion
11	Red, signature	Ca, Ti, Cr, Fe, Zn, Cd, Hg	Zinc white, calcium carbonate and/or calcium sulfate, chrome oxides, titanium white, Fe oxides, vermilion, Cd yellow

The cross-sections did not show any ground layer, because the pictorial layers were laid directly on top of the support. The results are shown in Table A02.02.

The yellow sample (BW1) collected on the background showed a single pictorial layer. In the SEM-EDS spectra, zinc was the main element, possibly associated to zinc white, but the small amounts of barium, likely as barium sulfate, cannot exclude the possible additional presence of lithopone. Small amounts of chlorine, sulfur and cadmium were also found, the latter probably linked to cadmium yellow. Moreover, Raman microscopy identified vermilion and PG7 (*Colour Index Generic Name* Pigment Green 7, *Colour Index Number* 74260, copper polychloro phthalocyanine).

In order to obtain the blue colour of the water, several small brushstrokes were applied close to each other. In the cross-section of BW2 the support is missing but it shows at least two pictorial layers. The results of SEM-EDS of the lower layer show zinc as the predominant element, possibly associated to zinc white. Very small amounts of calcium, barium and other elements were also present. The upper blue layer contained zinc, barium and sulfur as the predominant elements, suggesting the presence of zinc white and/or zinc sulfide and barium sulfate. FTIR analyses identified calcium carbonate and a drying oil as the organic binder. Zinc carboxylates were also identified at 1538, 1455, 1398 cm^{-1}. Additionally, Raman microscopy showed Prussian blue, ultramarine blue, barium sulfate and PG7.

Table A02.02. Summary of the analyses carried out on the cross-sections of *Bathing Women*, combining the results of FTIR, SEM-EDS and Raman microscopy for the pictorial layers.

Cross-section, number and colour	**SEM-EDS**	**FTIR (cm^{-1})**	**Raman (cm^{-1})**	**Pigment interpretation and chemical composition**
BW1, Yellow 	S, Ba, Cd, Zn, Hg	-	344, 288, 255 (cinnabar) 1536, 1345, 1290, 1216, 775, 738, 686 (PG7)	Zinc white (ZnO) Barium sulphate ($BaSO_4$) Lithopone ($BaSO_4$, ZnS)? Cadmium sulfide (CdS) Cinnabar (HgS) Phthalocyanine green, PG7 silicates
BW2, Blue 	Na, Mg, Al, Si, S, Fe, Ba, Zn	2920, 2852, 1735 (drying oil), 2090, 1409, 983 (Prussian blue), 1538, 1455, 1398 (Zn carboxylates), 1176, 1114, 1065, 1000 (barium sulfate), 1410, 872 (calcium carbonate)	2150, 2120, 2088, 546, 279 (Prussian blue), 986 (barium sulfate) 1100, 546, 260 (ultramarine blue) 1540, 1212, 772, 738, 688 (PG7)	Zinc white (ZnO) Barium sulphate ($BaSO_4$) Lithopone ($BaSO_4$, ZnS)?Prussian blue ($Fe_4[Fe(CN)_6]_3$) Ultramarine blue ($Al_6Na_8O_{24}S_3Si_6$) Phthalocyanine green, PG7 Drying oil Zinc carboxylates

Comparison with original Munch's artworks

Almost 1700 artworks are part of Munch's catalogue, because he was a prolific artist during all his lifetime [1]. As regards the support, cardboard was frequently used during the early period of the artist, particularly for landscapes. Although he preferred canvas, wood and cardboard were used especially for smaller paintings [2, 3], often without a preparation [1].

Following an evaluation of the published art technical studies, some pigments were distinguished on the basis of the period of time [1, 4–6] (Table A02.03). From 1885 to 1929, the main white pigment was zinc white, followed by lead white and barium sulfate. For the blue, artificial ultramarine blue was common, together with cobalt blue and Prussian blue, while cerulean blue was rarely used. Several yellow pigments were also experimented by the artist, as cadmium yellow, strontium yellow, yellow ochre, chromates (sometimes identified as chrome yellow, or indicated as probably lead chromate or zinc yellow), yellow lakes and synthetic yellow pigment (isoindoline). Emerald green, viridian and chrome green were used as green pigments, while later in his lifetime, around 1916, he utilised copper-based pigments and in one case green earth.

Most of the pigments found in this study correspond to the palette of the published works, but it can be asserted that green phthalocyanine was not found in the published art technical data, while it is present in the painting analysed in this study. However, this research should be considered not complete, because it is lacking the scientific investigation of artworks painted during the last period of Munch's lifetime.

Conclusion

All the pigments and binders identified were chronologically compatible with the art history of 20th century: *Bathing Women* could have been painted from 1936 due to the detected PG7. The artwork is compatible with Munch's lifetime, materials and technique, following a comparison with edited data. However, caution needs to be taken because the majority of the published data were collected with a different set of techniques. Furthermore, no information is available about art technical results for Munch's later period.

The presence of a signature, which is an element that can add value to an artwork, needs to be carefully evaluated. UV identified retouched areas at the bottom, and the analysis of the cross-section nearby the signature, as previously discussed, identified titanium white in the rutile form, which was commercialised in 1945, one year after the artist's death. However, if the painting was an original with a later addition (genuine or fraudulent) or if it is a forgery it cannot be discerned. This object was not unambiguously classified due to its controversial nature and also lack of published data on Munch's later paintings.

Appendix A.02

Table A02.03. Pigments identified on several paintings attributed to Munch are expressed in this table. Note that different scientific analyses were carried out.

		PAINTINGS											
		The sick child 1885-96	**The Scream 1893**	**Separation 1893**	**Madonna 1894**	**The Old man in Warnemunde 1907**	**The Scream 1910(?)**	**The history 1910-11**	**Chemistry 1909-16**	**New Rays 1909-16**	**Women Harvesting 1909-16**	**The Fountain 1909-16**	**The Human Mountain 1927-29**
White	Zinc white	✓	✓		✓	✓	✓		✓	✓	✓	✓	✓
	Lead white	✓	✓		✓	✓				✓	✓		✓
	Barium sulfate		✓										
Blue	Ultramarine blue	✓	✓		✓	✓	✓		✓	✓	✓	✓	✓
	Cobalt blue	✓							✓	✓	✓	✓	✓
	Prussian blue		✓		✓		✓	✓	✓		✓		
	Cerulean blue								✓		✓	✓	
Red	Vermillion	✓	✓		✓	✓	✓		✓	✓	✓	✓	
	Red lakes	✓	✓		✓	✓	✓		✓	✓	✓	✓	✓
	Red ochre	✓	✓								✓	✓	
	Umber	✓											
	Sienna				✓								
	Red lead						✓						
	Cadmium red												✓
Green	Emerald green	✓		✓					✓			✓	
	Viridian		✓			✓	✓						✓
	Chrome green								✓	✓			✓
	Cu-based green								✓		✓		
	Green earth											✓	
	Cadmium green					✓							
Yellow	Cadmium yellow	✓	✓	✓			✓		✓	✓	✓	✓	✓
	Chrome yellow								✓	✓		✓	
	Sr yellow									✓			
	Yellow ochre	✓			✓								
	Pb chromate	✓	✓		✓								✓
	Yellow lakes		✓		✓		✓						
	Zn yellow		✓										
	Isoindoline					✓							
Violet	Cobalt violet						✓		✓				✓
	Mn violet									✓	✓	✓	
Black	Carbon black	✓	✓		✓		✓						
	Bone black	✓											

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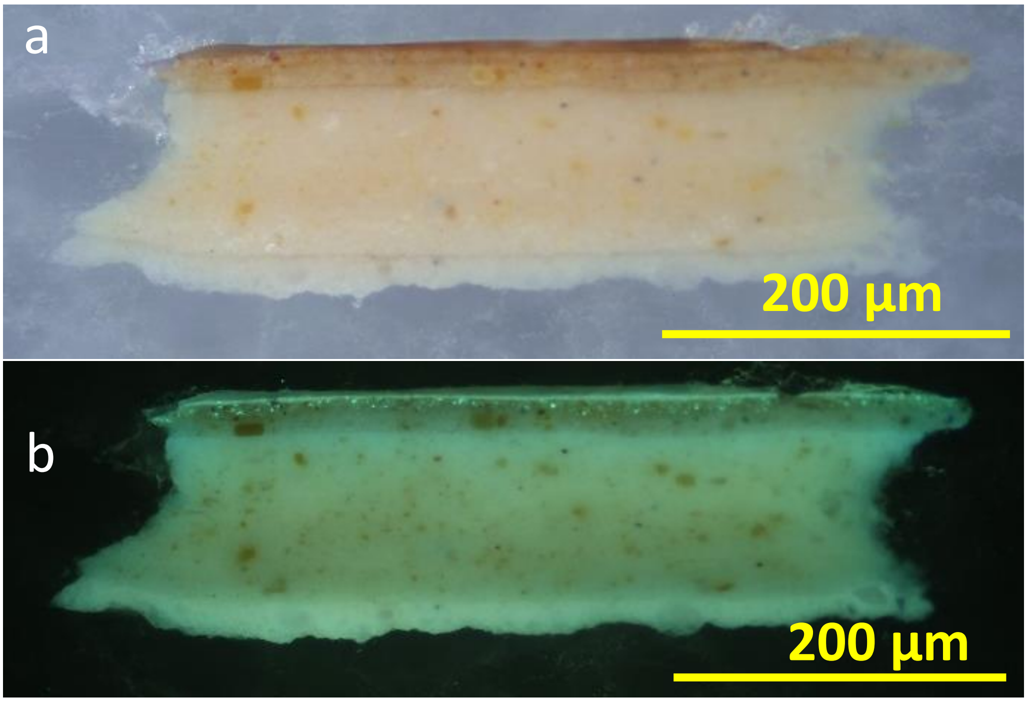
A.03 - Angel holding a *tabula ansata*

Scientific analyses on the cross-sections are expressed in the following tables, related to each sample analysed.

1. Yellow background



A03.01. Cross section of the yellow sample, a) visible light and b) UV fluorescence.

Table A03.01. Summary of the analyses carried out.

N.	Colour and thickness	Visual examination	SEM-EDS	Raman
4	Yellow, 10-15 µm	Two different varnishes, probably not original but due to restoration	-	-
3	Yellow, 15 µm	Yellow matrix with yellow, red and rare and fine blue grains	Na, Si, Pb, Zn	-
2	Yellow, 20 µm	Yellow matrix with yellow and light yellow grains; presence of fine and rare blue grains	Na, Al, Si, Pb, Sb	127 (Naples yellow) 546 (ultramarine blue) 1050 (lead white)
1	Light yellow, 100 µm	Light yellow matrix with yellow and translucent grains	Pb, Sb, Fe	125, 300, 518, 976 (Naples yellow) 108, 1050 (lead white) 148, 210, 315, 658 (rosiaite)
0	White, >20 µm	White matrix with big and translucent grains	Pb	1050 (lead white)

2. Shadowed flesh tone

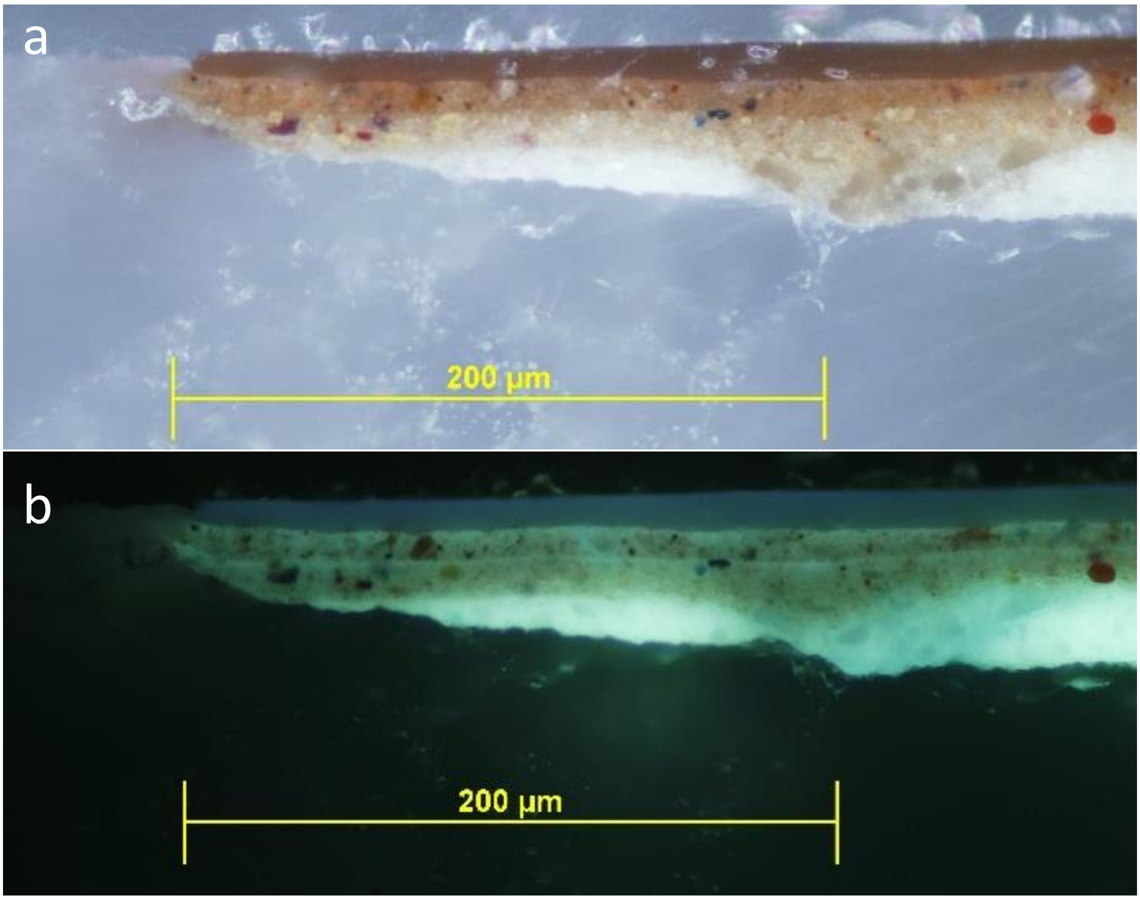


Figure A03.02. Cross section of the flesh tone sample, a) visible light and b) UV fluorescence.

Table A03.02. Summary of the analyses carried out.

Nr.	Colour and thickness	Visual examination	SEM-EDS	Raman
3	Yellow, 20 µm	Varnish	-	-
2	Brown, 20 µm	Brown matrix with red, brown, blue and transparent grains	Na, Al, Si, Pb, S, Ca, Fe	127 (Naples yellow)
1	Pink/ brown, 40 µm	Pink matrix scattered with yellow, blue, red and transparent particles	Na, Al, Si, Pb, S, Ca, Sb, Fe, Cu	125 (Naples yellow) 658, 129 (rosiaite) 225, 291, 406, 610 (hematite) 548 (ultramarine blue)
0	White, >50 µm	White matrix with large, translucent grains	Mg, Al, Si, Pb	1050 (lead white)

3. Green background

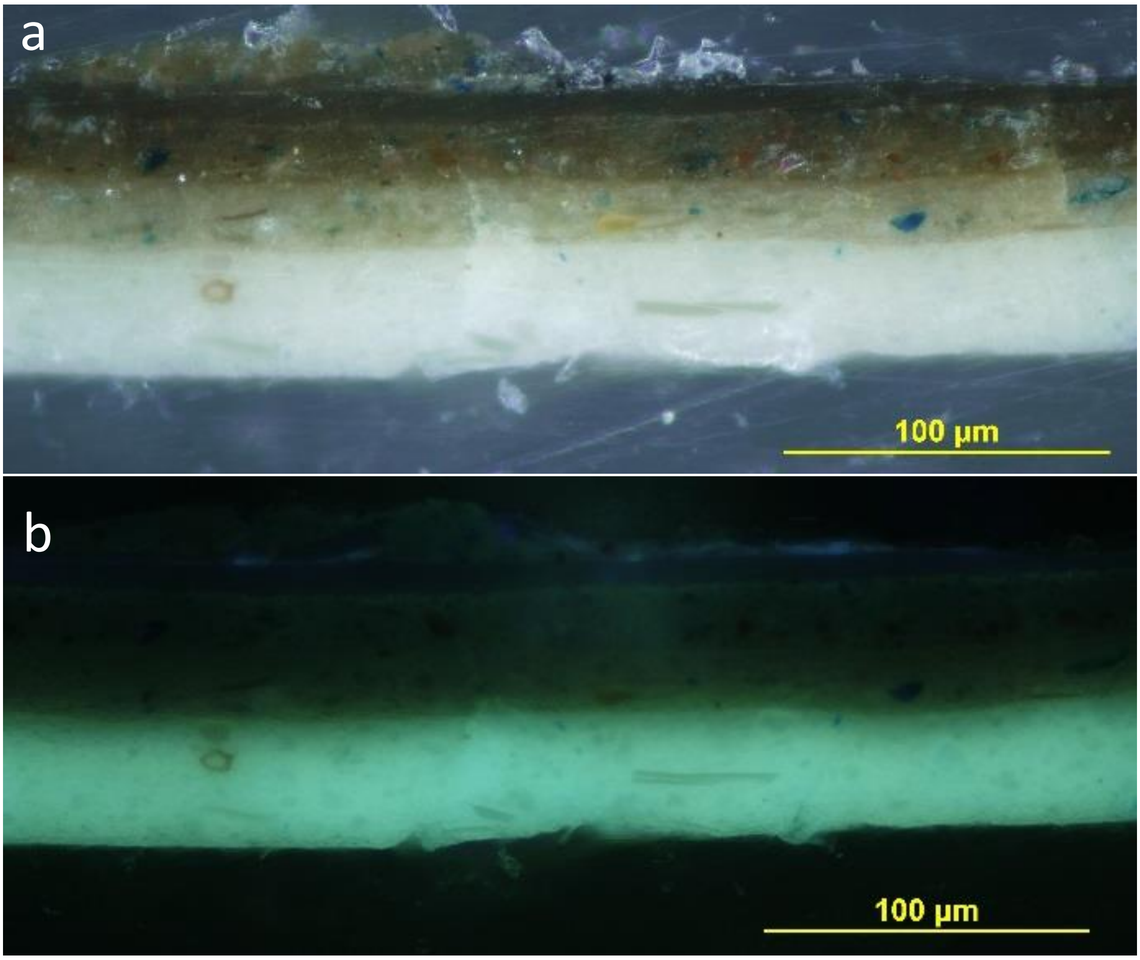


Figure A03.03. Cross section of the green sample, a) visible light and b) UV fluorescence.

Table A03.03. Summary of the analyses carried out.

Nr.	Colour, thickness	Visual examination	SEM-EDS	Raman
4	Green, 20 µm	Retouched layer	-	-
3	Yellow, 20 µm	Varnish	-	-
2	Green, 40 µm	Green matrix with brown, blue and transparent grains	Na, Mg, Al, Si, Pb, S, Ca, Fe,	548 (ultramarine blue) 224, 290, 408 (hematite)
1	Light green, 30 µm	Green matrix with blue, yellow and transparent grains	Na, Mg, Al, Si, Pb, S, Ca, Sb, Fe, Cu	130, 300, 515, 658 (rosiaite) 546 (ultramarine blue) 140 (Pb oxide)
0	White, >50 µm	White matrix with big and translucent grains	Na, Mg, Al, Si, Pb, Ca	1050

Conclusion

The white preparation is directly applied on the wooden support and mainly consists of lead white and possibly silicates as extender.

The pigments identified are the following:

- Red: red ochres.
- Blue: ultramarine blue.
- Green: mostly obtained with a mixture of blue and yellow, and probably with an addition of copper-based pigments such as malachite or verdigris.
- White: lead white, zinc white.
- Yellow: Naples yellow, possibly yellow ochres.

In order to achieve a particular hue, the artist painted at least two pictorial layers (for the yellow sample the layers are three) of different composition. In particular, the lower layer always contains Naples yellow, but this pigment is not identified in the final layer, which is richer in ochres.

The binder is suggested to be a drying oil due to the yellowish UV fluorescence, but further analyses are required to confirm this hypothesis.

Appendix B - Ground layers

The ground is the first layer applied on top of the support. The study of this layer is extremely important, as it provides a first discriminating element for chronological and possibly geographical context. The function of the preparation layer is to smooth the roughness of the support, so to make it suitable for the pictorial layers[23]. In addition, it helps in decreasing the absorption from the binder of the upper layers, which guarantees the cohesion of the pigments and therefore preserve the original colours. Moreover, a ground should have a good flexibility in order to bear the changes of the support due to changes in temperature and humidity.

The preparation can have more than one layer; generally, the lower layers are characterised by a higher degree of roughness and thickness in comparison to the smoother and more uniform upper ones. The materials used come from a regional source, because their consumption was relatively higher and thus the price became a very important factor.

On top of the ground, a layer called priming (or imprimatura) can be present. It offers several functions: for instance, it creates an optical base for the pictorial layers, makes the ground smoother and facilitates the spreading of the brushstrokes.

In the end, pictorial layers, made of a mixture of pigments and binders, are laid on the surface, the number of which varies on the basis of the final optical effect that an artist wants to achieve and possibly of the binder, as for instance an egg binder dries faster than a lipid one. Pigments can be inorganic or organic, natural or synthetic, and their formulation and use during history has been well documented, as for instance particular pigments were introduced in the art market in specific years, therefore providing evidence for a chronological context.

In this appendix, materials used for grounds are summarised accordingly to the centuries and specific locations, with a focus on Italian and Northern European contexts.

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15th century

WHITE GROUNDS

From double layer to single layer during the century[1]

ITALY

<u>Materials</u>: mix of gypsum and anhydrite (Venetian area: wholly gypsum)[2]
Gesso grosso calcium sulfate, anhydrite (usually south of the Appennini)[1]
Gesso sottile: calcium sulfate, dy-hydrate (usually north of the Appennini)[1]

Tuscany School: two ground layers until the end of the century[1]

PRIMING: animal glue, until the beginning of 16th century[3]
Verdaccio: used under flesh tones[*]

EUROPE

North Europe
<u>Materials</u>: calcium carbonate + animal glue[1,2]
Thinner layer in comparison to Italian grounds

Alpine regions, Burgundy, Bohemia, Poland
Dolomite[1]

Germany
Sometimes addition of gypsum or lead white to chalk[1]

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[*] This underpaint was discussed by Cennino Cennini (*Libro dell'arte*, chapters 53 and 147). The colour consisted of a mixture of yellow, white, black and red pigments or green earth and a white pigment, and it was especially used to obtain the shadings of the flesh tones, as a greenish hue would make them more realistic. In the 16th century, Vasari also describes a mixture or green and black earth, called *verdaccio*, used for the shadings and under the flesh tones on frescoes (*Vite degli uomini illustri*, chapter 25).

16th century

	WHITE GROUNDS (1500 – 1575)	COLOURED GROUNDS (1575-1600)
ITALY	*Panel* Materials: calcium sulfate (both di-hydrate and anhydrite) + animal glue[2,4,5] *Gesso grosso* (larger particles size), *gesso sottile* (finer particles size) Notes: Rome and Florence: both types; Venice: gypsum[5]; some regions in the north of Italy: dolomite[5] *Canvas* Materials: gypsum + animal glue + oil[5] Notes: canvas is used since the half of 16th century	Colours: grey, red, brown[6] Materials: gypsum, earth pigments, black pigments, vermilion, lead-based compounds Notes: sometimes double layer (spread in the 17th century): 2- Lead white, carbon black, ochres, earth and umber pigments, red lead, vermilion 1- Earth and umber pigments, calcium carbonate, lead white, red lead, carbon black
	PRIMING - First half 16th	**PRIMING** - Second half of the 16th century
	White priming[3] Materials: lead white + oil or Lead white + oil + Pb-Sn yellow (Florence and Ferrara) **Coloured priming**[3] Colour: lightly coloured Pink, yellow, beige, grey (North Italy, Venice, Rome)	**Coloured priming**[3] Colour: deep-tone or black Materials: lead white, diverse black pigments, earth pigments, ochres, Pb-Sn yellow; less common red lead and vermilion Notes: beginning of 1500: North Italy (Mantova, Ferrara, Brescia) ~1540: central Italy ~1550 onwards: Venice

	WHITE GROUNDS (1500 – 1575)	COLOURED GROUNDS (1575-1600)
EUROPE	**North Europe** Materials: calcium carbonate[4]	Since 1550
	Iberian Peninsula Materials: calcium carbonate or sulfate[5] (anhydrite and di-hydrated form[7])	Since 1575

17th century

GROUNDS

ITALY

Colours: red, grey/beige or brown

Materials:

- Brown earth tones + chalk[8] and in minor amount gypsum, red lead and lead white (Bologna area: Sienna or umber)[8,9]. Jarosite as impurity[9].
- Red-brown ground made of Fe oxides and Ti (anatase)[10]
- Lead white + earth tones and carbon black[9]
- Brown-beige ground made of quartz, chlorite, K-based phases, calcite (small amounts of dolomite and kaolinite). FeS (Foraminifera shells)[10]

Notes: single layer or double layer

EUROPE

The Netherlands

Colour: Usually reddish colour[9]

Materials:
chalk + grey layer (priming)[6]
Chalk-based[9]
Chalk + scattered pigments: grey, yellow, red ochres)[9]

Notes:
Single or double layer[9]
Since 1650: darker and thinner grounds

London
Colours: brown, red or yellow colour[9]

Materials[9]: chalk + earth tones
Or Fe oxides + silicates, less amount of chalk

Czech Republic[10]
Kaolinite-rich ground + quartz, Fe oxides (Ti), as Czech bole
Or
Quartz + kaolinite, illite, hematite (less amount of Ti), as “German bole”
(widely spread also in Europe and France)

France

Colours: white, faintly tinted or red-brown coloured

Materials[6,11]:
White: Chalk-based
Faintly coloured: Chalk + scattered pigments (lead white, red lead, earths, red or yellow ochre) or brown earths
Red: Chalk + Fe oxides
Red: earth tones (brown, red, yellow) + small amount of chalk
Brown: earth tones + chalk and lead white
Lead white + earth pigments, carbon black
(Paris areas: barium sulfate as extender of red ochres, between 1620-80[11–13]
Lorraine region: earth tones + chalk[9])

Notes: single layer or double layer: lower layer: red colour; upper layer: various colour (yellow, grey), lead white[6]

18th century

GROUNDS & PRIMING

ITALY

1700 – 1750

Italy
Colour: dark brown-reddish colour:
Materials: ochres, red lead
Notes: single layer

Priming
Sometimes a lead white layer is applied on top

1750 - 1800

Neoclassicism

Colour: white[1,14]

Materials: double layer[1]:
2- lead white or calcium carbonate + ochres
1-chalk + lead white / or light brown

Notes: also single ground[14]

EUROPE

Europe 1720 – 40

Colour: warmly coloured grounds (ochre or reddish tones)[1]

Materials: double layer[14]:
Earth layer + top lead white

Notes: lead white as second upper layer[14]

The Netherlands

Materials: double oil layer (used since 17th century)[15]
2- light layer: grey
1- dark layer: chalk or ochres

Light layers, i.e. grey, as second upper layer

France

Materials: double layer:
2- various colour
1-red layer

Light layers, i.e. grey, yellow, as second upper layer

19th century

WHITE GROUNDS

EUROPE

Colour: white, light coloured

Materials:
Lead white, lead white + chalk, zinc white (end of the century)[1,14]
But also pure barium sulfate or chalk (especially in the second half of the century)
+ earth colours and different blacks added to adjust the tone

Fillers: barium sulfate, calcium carbonate, gypsum, kaolin[1]
These fillers avoid the absorption of the oil from the ground (problems of yellowing and darkening)

Binders: animal glue and/or oil; alternate binders: casein, starch, egg yolk, gums[1].

Notes: Environmental pollution: lead white becomes PbS, zinc white is a replacement option[1].
Expansion of the art market: grounds already applied on canvases before selling them[1]

20th century

WHITE GROUNDS[1]

	1920s	1950s	1960s
EUROPE	Materials: titanium white *Extenders*: chalk, barium sulfate, calcium sulfate, kaolin, talc, silica	Materials: acrylic binder Notes: High flexibility, high absorbance power, less yellowing, paint layers do not crack. Regulation for health and safety: modification of the grounds (since 1950s lead white is not used anymore)	Materials: alkyd binders (from the 1930s as household paint) Notes: fast drying, good durability and hardness, yellow less

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