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Spectroscopic Analyses of Blue Pigments in the Manoscritto Parmense 3285 from the 14th Century

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Abstract: During the restoration and digitalization intervention of the Manoscritto Parmense (Ms. Parm.) 3285 codex, a 14th-century illuminated volume that contains the three books of Dante Alighieri's Divina Commedia belonging to the Biblioteca Palatina of Parma, the deposits present in the center of some bifoliums were removed using soft bristle brushes and collected. A preliminary observation of these deposits with a stereomicroscope allowed the detection of some pigment grains of different colors, likely detached from the full-page illuminations at the beginning of each book. These grains of the pigments were then analyzed in the Bologna ENEA Research Centre through Scanning Electron Microscopy (SEM), EDX microanalysis, and micro-Raman spectroscopy, allowing the identification of the minerals or the compounds used as pigments. Consequently, some pigments that were commonly used in the Middle Ages such as gold leaf, typically employed in illuminations and the decoration of heading initials, cinnabar red, and different types of blue pigments, including traces of lapis lazuli and azurite, were identified.

Keywords: SEM-EDX; micro-Raman spectroscopy; illuminated manuscript; pigment analysis

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1. Introduction

The object of this study is the 14th-century Manoscritto Parmense 3285, belonging to the Biblioteca Palatina of Parma, a manuscript that contains the *Divina Commedia* (Divine Comedy) by Dante Alighieri. The Divine Comedy is an Italian poem completed around 1321, describing Dante's travels through Hell, Purgatory, and Heaven, and is widely considered a pre-eminent work in Italian literature and one of the greatest works of world literature. The manuscript, originating from a commercial scriptorium in Florence renowned for the production of Divine Comedy copies, represents one of the first copies of the poem and, like most medieval manuscripts, is handwritten on parchment and is adorned by illuminations, a complex and expensive process that was usually reserved only for special books [1–3].

Three magnificent illuminated pages, corresponding to the incipit of the three books into which the poem is divided, are the most valuable decoration of the manuscript. The decoration features many colors such as blue, red, green, pink, brown, and black, and includes a figurative initial letter and a full-page frame with illustrations referring to the content of the book.

The text is written in brown ink, while red ink is used to indicate the number of paragraphs, and verses are highlighted with a yellow capital initial in relief. Finally, the first letters at the beginning of each paragraph are alternatively in red or blue pigments and adorned with a filigree of the opposite color, a typical decoration of all 14th-century Western manuscript production [4,5] (Figure 1).

Figure 1. The illuminated page at the beginning of the Paradise chapter (**A**) and the first letter of a paragraph (**B**).

The manuscript was in a precarious state of conservation: the main problems were found in the binding, which was not original and was too rigid at the spine, making it difficult to open the book. Furthermore, the excessive amount of adhesive used for this binding also caused the contamination of numerous pages, causing damage to the miniatures. In particular, the illuminated page of the Paradise was more damaged than the others because the adhesive had transferred some portions of the miniature onto the preceding page (Figure 2).

Figure 2. The transfer of miniature portions onto the preceding page (**A**) and the detachment of miniature portion (**B**).

The manuscript was restored and digitalized in 2021. During the restoration, which required the temporary disassembling of the book, the dust deposits present between the pages were collected, and some grains of pigments were found (Figure 3). These grains were analyzed using FEI (Hillsboro, OR, USA) Scanning Electron Microscopy, Oxford Instruments (Abingdon, Oxfordshire, UK) EDX microanalysis, and micro-Raman spectroscopy at the ENEA Bologna Research Center. The combination of these complementary techniques allowed for very effective identification of the minerals present in the samples, even when analyzing minimal amounts of material [6–8], allowing the identification of the pigments and their nature without ambiguity.

Figure 3. The collection of dust deposits found between the pages.

Even though it is not possible to determine with precision the exact provenance of these fragments, i.e., from which area of the miniatures they derive, their analysis reveals a lot about the artistic value of this work and, in particular, about the history of the interventions that it has undergone over the centuries, especially in the modern era.

The present work focuses on blue pigments because this color often derives from materials of economic value that can vary greatly, from very common and cheap to very rare and expensive. The former were used for less valuable works, but the presence of some of the expensive ones may indicate the importance that was already attributed to a certain masterpiece at the time of its commissioning. Valuable materials certainly indicate that a certain work was intended for illustrious people or important customers, capable of paying the cost.

Also, the red pigments have been investigated, which were unambiguously identified as Cinnabar, as well as the gold leaf used for the gilding of the illuminated page.

Furthermore, during this work, grains consisting of a different and more recent pigment were identified: the Prussian blue. This pigment was synthesized centuries after the period in which this manuscript was created, and this proves that a restoration intervention was carried out in more recent times, probably at the beginning of the 20th century, as a record of the intervention was found in the archives of the Biblioteca Palatina library.

This result, in itself, underlines the importance of instrumental analyses carried out on ancient masterpieces, both from the point of view of conservation and possible restoration interventions and to understand their conservation history and the rationale behind the previous restoration interventions.

2. Materials and Methods

The samples were preliminarily observed with a Wild stereomicroscope for the selection of the grains to be analyzed: fragments of gilding, red pigment, and different blue pigments were isolated from dust deposits and glue particles.

The grains were positioned delicately on a SEM stub, and the analysis was performed without any further preparation. The same stub was then used to perform the Raman spectroscopy without changing the support to preserve the sample integrity.

Samples were initially analyzed using a FEI (Hillsboro, OR, USA) Quanta InspectS Scanning Electron Microscope coupled to an Oxford Instruments (Abingdon, Oxfordshire, UK) Xplore microanalysis: observation of the pigment grains was carried out at different magnifications ranging between 500× and 2000× using both secondary electrons (SE) and backscattered electrons (BSE) detectors at a 10 nm working distance, with energy ranging from 10 to 20 KeV. The elemental analysis was carried out in the most significant areas of the samples using AZTecLive 6.1 platform software. Compositions were determined by averaging the values found in three different points of the samples.

The Raman spectra of the compounds were acquired by a BWTEK (Plainsboro, NJ, USA) i-Raman plus spectrometer, equipped with a 785 nm laser to stimulate Raman scattering, which were measured in the range of 100–3500 cm^{-1}, with a spectral resolution of 3.5 cm^{-1}. The measurement parameters, acquisition time, number of repetitions, and laser energy were selected for each sample to maximize the signal-to-noise ratio. For each spectrum, a reference acquisition was previously made with the same parameters to subtract the instrumental background.

3. Results and Discussion

Figure 4 shows the typical appearance of the pigment grains on which analyses have been performed, seen using a stereomicroscope (A) and an SEM (B).

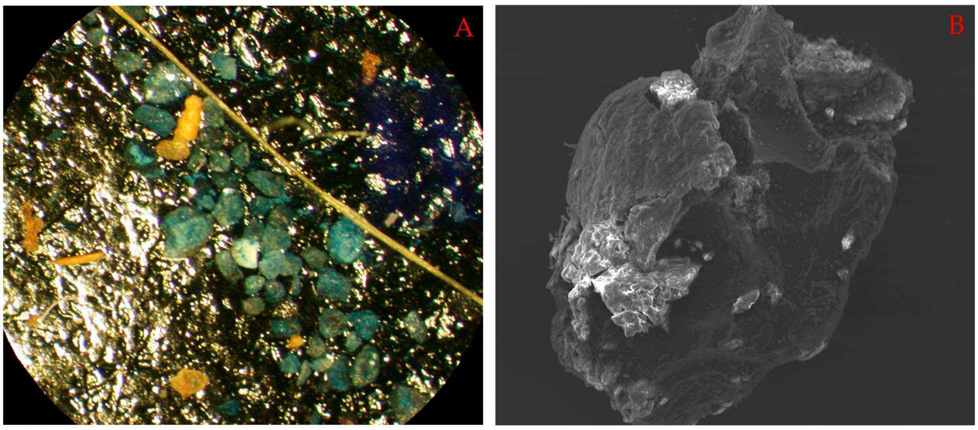

Figure 4. Stereomicroscope image of the pigment grains (40×) (**A**) and SEM image of a pigment grain (500×) (**B**).

The microanalysis performed on the samples allowed the identification of the chemical elements present and, starting from these, the classification of the grains into gold pigment, red pigment, and three blue pigments, characterized by different chemical compositions. This made it possible to develop the first hypotheses regarding the pigments used for the creation of the illuminations, which would be confirmed with the following Raman analysis. Since many of the analyzed blue samples contained grains of different pigments, a new selection of the grains was necessary before carrying out Raman analyses to make the sample homogeneous and facilitate the interpretation of the acquired spectra.

Raman spectroscopy is a very powerful tool, allowing the identification of the pigments without ambiguity by the position of their peaks, through comparison with specific databases [9] or with the scientific literature in the field [10,11]. In this study, since the samples were analyzed as they were, the obtained spectra showed not only the peaks associated with the pigment but also the peaks due to the binders that were used to make them adhere to the support, which introduced some challenges in their correct identification.

However, the combination of elemental composition results and spectral analysis allowed for the certain recognition of the analyzed grains and the identification of the pigments: gold leaf, cinnabar, azurite blue, natural ultramarine blue, and Prussian blue.

Although there was little doubt that the golden parts of the decorations were realized using gold leaf, the SEM image obtained with the backscattered detector (Figure 5) and the microanalysis carried out on the bright areas of the image (Figure 6) helped resolve doubts and confirmed the use of this precious element in the decoration.

In Table 1, the presence of gold clearly revealed the nature of the gilding, while aluminum, silicon, and iron are due to the use, as a base for the gold leaf, of the Armenian bole, an earthy clay, usually reddish, native to Armenia but also found in other places, which was applied to give the gilding greater brilliance and a warmer tone.

Table 1. Measured average composition of the golden pigment.

Element	Weight %	Atomic %
C	17.69	59.37
O	8.97	22.59
Al	0.79	1.19
Si	1.35	1.94
Fe	0.64	0.46
Au	70.56	14.44

Figure 5. SEM image of the golden pigment (BSE detector, 1000×).

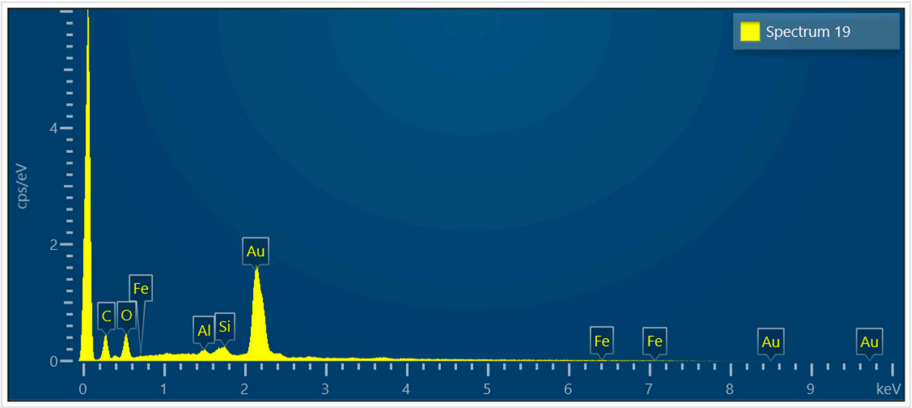

Figure 6. Microanalysis spectrum of the golden pigment.

The red pigment was easily identified as cinnabar, a bright red mineral also named vermilion, consisting of mercury sulfide, which is the source of its brilliant color, through the detection of mercury and sulfur in its grains, as shown in the microanalysis spectrum of Figure 7 and the element concentrations reported in Table 2. Cinnabar is one of the most common pigments used by humans since ancient times, with its use dating back to the Neolithic age, as reported by Pannocchia et al. [12]. The detection of lead and carbon can be related to the presence of white lead, a thick, opaque, and heavy white pigment composed of basic lead carbonate, the most widely produced white pigment from antiquity until the 19th century. Lead white was frequently used to produce tints of other colors: in combination with red and brown pigments, for example, it was commonly used to create flesh tones [13].

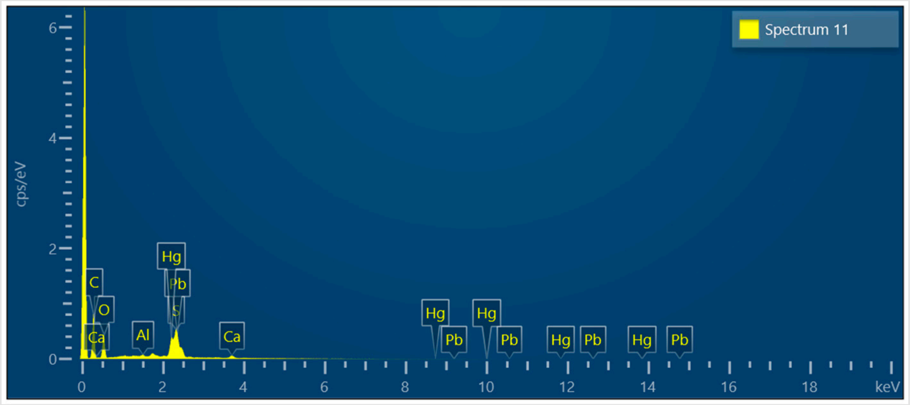

Figure 7. Microanalysis spectrum of the red grain.

Table 2. Measured average composition of the red grain.

Element	Weight %	Atomic %
C	48.15	73.51
O	18.88	21.64
Al	0.34	0.23
S	2.58	1.47
Ca	1.20	0.55
Hg	15.93	1.46
Pb	12.92	1.14

The first blue pigment was azurite, a deep-blue mineral pigment derived from a naturally occurring copper carbonate, formed through the weathering of ore deposits. Its chemical formula is $2CuCO_3 \cdot Cu(OH)_2$. It has been used as a pigment since antiquity, even if it is not very stable in air. During the Middle Ages, it was the most prevalent blue pigment in Europe because it was a common mineral at the time, which had been mined since the 12th century [14]. Interestingly, artists had the opportunity to modulate the intensity of the color by using specific binders, such as egg yolk, which slightly shifts the color toward green [15], or by grinding other minerals together and mixing thoroughly.

Actually, in the present work, microanalysis, performed on several grains, revealed the simultaneous presence of copper, which is the element that characterizes azurite, and of a small quantity of lead that can be related to the white lead pigment, $2PbCO_3 \cdot Pb(OH)_2$, probably used in combination with azurite to give the color a lighter tone. Trace amounts of aluminum, silicon, and calcium were also detected and are attributable to the presence on the surface of the pigment grains of dust residues, which constituted the largest part of the particles collected from the manuscript during the restoration operations.

Figure 8 shows a typical EDX spectrum of an azurite grain, while Table 3 reports the element concentrations.

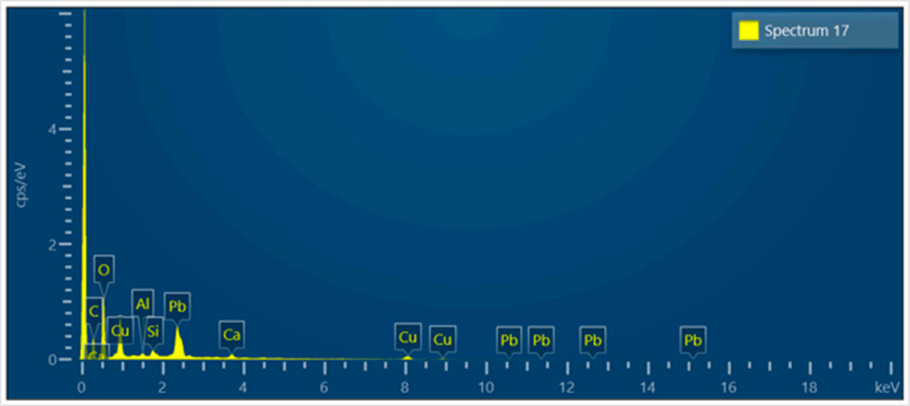

Figure 8. Microanalysis spectrum of azurite.

Table 3. Measured average composition of the azurite grain.

Element	Weight %	Atomic %
C	29.93	45.34
O	44.13	50.17
Al	0.56	0.37
Si	0.98	0.63
Ca	1.13	0.51
Cu	4.66	1.33
Pb	18.62	1.64

Raman spectroscopy also confirmed the identification, as the main bands of this pigment were detected at 403 cm^{-1} and 1098 cm^{-1}, as well as two characteristic less intense signals between 750 and 950 cm^{-1} (Figure 9).

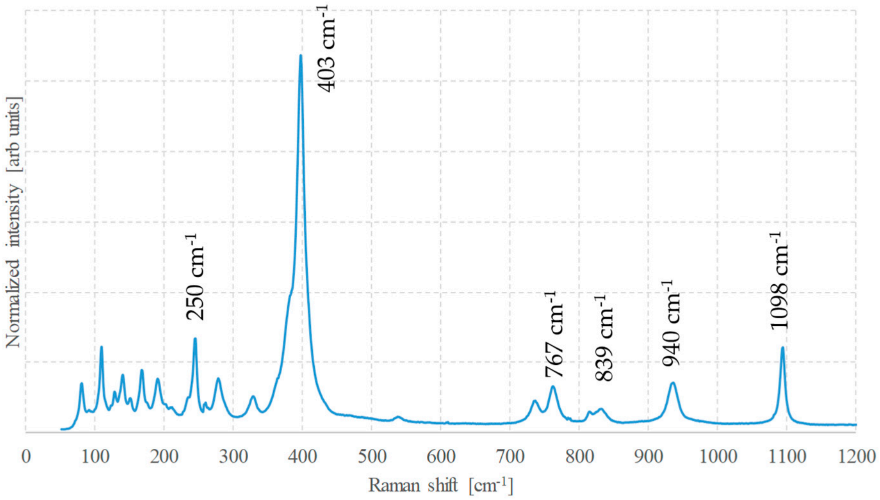

Figure 9. Raman spectrum of azurite.

Being a basic carbonate, where copper II cations are linked to carbonate and hydroxide groups, the Raman spectrum of azurite presents many bands related to the vibrations of the $CO_3{}^{2-}$ group [16]. Carbonate is a non-linear species and thus has six normal modes of vibration. As a free ion, it has three Raman active modes: ν_1, a non-degenerate symmetric stretch (A'_1) at 1064 cm^{-1}, ν_3, a doubly degenerate asymmetric stretch (E_1) at 1415 cm^{-1}, and ν_4, a doubly degenerate asymmetric (in-plane) bend (E_1) at 680 cm^{-1}. The last two are also IR–active. The mode ν_2, a non-degenerate symmetric (out of plane) bend, is only IR active, but in solids carbonate, due to a reduction in symmetry, it can be also Raman active, despite being normally quite weak. In addition to these main spectral features, solid carbonates present vibration modes related to M-O from the interactions between the cation (M) and the O of CO_3^{2-} group and of OH^- if it is present in the structure.

In particular, the azurite spectrum is characterized by several bands. Those below 600 cm^{-1} are attributed to the translations of (Cu, CO_3).

Azurite has a characteristic intense band at 403 cm^{-1}. The ν_1 symmetric stretching band of the carbonate ion is observed at 1098 cm^{-1}, which is at a higher wavenumber than the free ion. One band is observed in the Raman spectrum of azurite at 767 cm^{-1} and is assigned to the ν_4 mode, i.e., again at a much higher wavenumber than the same in the case of free ion, due to lattice interaction. The band at 835 cm^{-1} has been assigned to the ν_2 symmetric bending vibration. Many bands with different intensities are observed in the lowest spectral shift of the Raman spectrum of azurite. These Raman lines are assigned to the lattice modes. The O-H out-of-plane bending mode of azurite was reported at 939 cm^{-1}. The Raman band assignments were also compared and confirmed with the Raman Spectroscopic Library of Natural and Synthetic Pigments by Bell, Clark, and Gibbs [9].

The second blue pigment found is the finest and most expensive ultramarine blue, a deep blue pigment obtained by grinding into a powder the lapis lazuli rock, which contains the blue lazurite mineral, a complex sulfur-containing sodium silicate with the chemical formula $3Na_2O \cdot 3Al_2O3 \cdot 6SiO_2 \cdot Na_2S$, otherwise written as $Na_8[Al_6Si_6O_{24}]S$ [17–19].

Its use in some of the illuminations of the Ms. Parm. 3285 manuscript was confirmed by both elemental analyses, which revealed the presence of sodium, aluminum, silicon, and sulfur. Figure 10 shows the EDX spectrum collected on a grain of this pigment, and Table 4 shows the average composition.

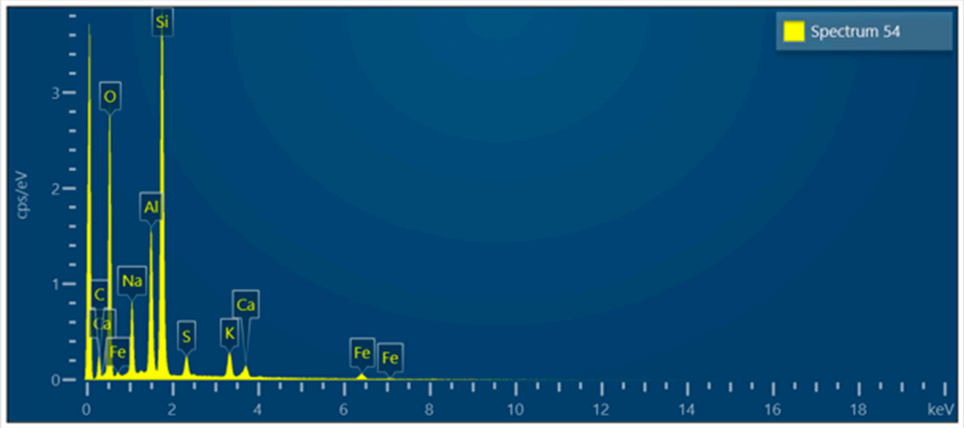

Figure 10. Microanalysis spectrum of natural ultramarine blue.

Table 4. Measured average composition of the ultramarine blue grain.

Element	Weight %	Atomic %
C	18.26	26.72
O	46.87	51.49
Na	5.31	4.06
Al	6.80	4.43
Si	17.69	11.07
S	1.16	0.64
K	1.84	0.83
Ca	0.91	0.40
Fe	1.16	0.37

Lazurite is easily identified through Raman spectroscopy by the presence of a strong band centered around 550 cm^{-1}, which is related to sulfide ions stretching. Another, weaker band reported in the literature [20] at 1096 cm^{-1} was not observed due to the strong fluorescence of the grain (Figure 11). The characteristic band at 548 cm^{-1}, together with the compositional analysis, allows an unambiguous identification [21].

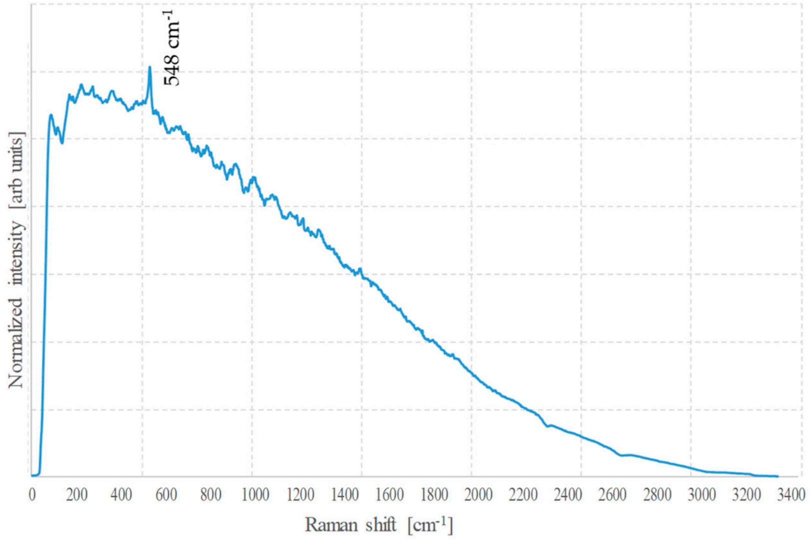

Figure 11. Raman spectrum of natural ultramarine blue (lazurite).

However, whereas Lazurite, which is responsible for the intense blue color of lapis lazuli, is a mineral with a specific composition, this pigment can contain many secondary phases and accessory minerals, depending on its geological and geographic origin, including calcite, pyrite, amphibole, pyroxene, sodalite, forsterite, muscovite, and wollastonite, among others. These minerals may play an important role in the spectroscopic properties of lapis lazuli, starting from the fact that they can induce strong fluorescence, as noted in the reported spectrum. The presence of transition metals in several of these secondary minerals can induce absorption through the transition metal d-orbital states, resulting in strong fluorescence with vibronic coupling. Furthermore, even the majority of binders, which are substances of natural and organic origin, such as egg yolk, isinglass, or glue from other animals, normally present spectra with strong fluorescence [21].

In any case, the lapis lazuli stone itself was relatively inexpensive, the long-standing importation of the raw material from the Afghanistan mines to Europe—from which the name ultramarine (overseas) derives—and the lengthy process to produce the pigment made it quite valuable: high-quality ultramarine was said to be as expensive as gold, and thus its use was limited to very precious artworks, highlighting that this manuscript at the time of its realization was already considered precious and intended for an important commission [22].

The final blue pigment that was identified is Prussian blue, a synthetic and stable pigment with a dark blue hue produced starting in the early 18th century by the oxidation of ferrous ferrocyanide salts, with the chemical formula $Fe_4[Fe(CN)_6]_3 \cdot x\, H_2O$. Prussian blue can be easily made and is inexpensive, nontoxic, and intensely colored. Thus, it was adopted as a pigment very soon after its invention and was almost immediately widely used in oil paints, watercolors, and dyeing [23–25]. Figure 12 shows the typical EDS spectrum collected on a grain of Prussian blue, and Table 5 shows the average composition.

The presence of iron is a strong indication of the nature of this pigment. The measured content is relatively low, but it must be kept in mind that the analyses were carried out on obviously polyphasic grains, and the pigment is only one of the present phases.

Raman spectroscopy is a powerful tool in this case as well, and the identification of the pigment was confirmed due to its unambiguous spectral features. Figure 13 shows the Raman spectrum of a grain. It is very interesting to note the presence of characteristic bands around 2150 cm^{-1}, i.e., in the typical area of triple bonds [26].

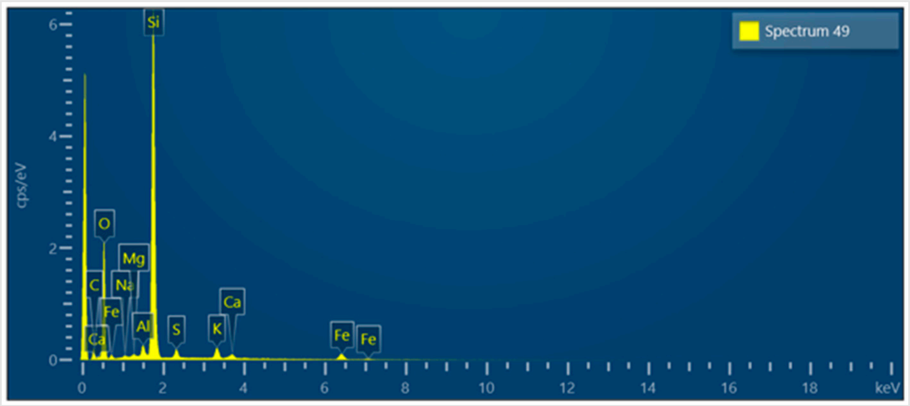

Figure 12. Microanalysis spectrum of Prussian blue.

Table 5. Measured average composition of the Prussian blue grain.

Element	Weight %	Atomic %
C	21.80	31.77
O	43.71	47.83
Na	0.22	0.17
Mg	0.20	0.14
Al	0.85	0.55
Si	27.88	17.38
S	0.94	0.51
K	1.46	0.66
Ca	0.91	0.25
Fe	1.16	0.74

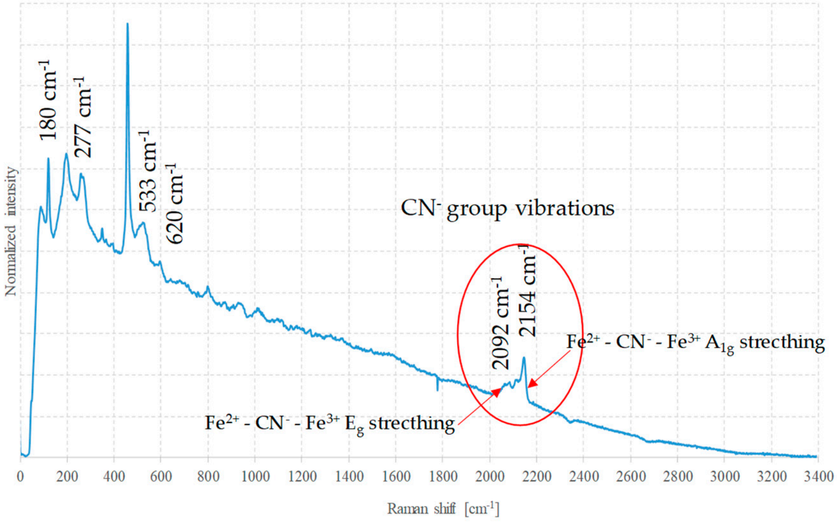

Figure 13. Raman spectrum of Prussian blue.

Prussian blue exhibits stretching vibrations of the C≡N bond between 2070 and 2200 cm^{-1}. In the solid state, the C≡N groups have different chemical environments and are coordinated differently by iron atoms, resulting in the observation of distinct bands. The main peak around 2154 cm^{-1} corresponds to the $1Ag$ $\nu(CN)$ stretching. This peak presents a shoulder towards lower wavenumbers at 2123 cm^{-1}, which is typical of CN$^-$. The second peak is observed at around 2100 cm^{-1} and corresponds to the Eg mode of the $\nu(CN)$ stretching vibration.

The bands in the wavenumber region between 450 and 620 cm^{-1} are attributed to Fe–C stretching vibrations, whereas those in the region between 190 and 340 cm^{-1} are due to Fe–CN–Fe bond deformation vibrations. Another shoulder, present at about 180 cm^{-1}, is characteristic of C–Fe–C deformations [27].

In addition to these clear signals attributed to the pigment, other signals are also present, including a narrow, intense peak at about 420 cm^{-1} and weaker ones that are not due to Prussian blue. It should be again kept in mind, however, that in this case, the pigment grains are immersed in a matrix mainly composed of organic binders. The contribution of this matrix cannot be neglected, but it does not prevent the identification of the pigment.

The hypothesis regarding the detection of this pigment, which was discovered about four centuries after the creation of Ms. Parm. 3285 and, therefore, not imaginable before the execution of the analyses, was evaluated with extreme attention.

Despite the presence of silicon and traces of many other elements that can be related to dust particles, the rather high concentration of iron highlighted by the microanalysis, which can be linked to a small number of blue pigments, combined with the clear peaks in the Raman spectrum at a wavelength of around 2100 cm^{-1}, which can be unequivocally attributed to the presence of the $C{\equiv}N$ group, allowed for the definitive identification of the grains as Prussian blue pigment [28].

4. Conclusions

The identification of pigments used in historical paintings and manuscripts is interesting and undoubtedly useful both for art historians and restorers, as well as from the point of view of the development of instrumentation and measurement techniques. The results of the analyses carried out on the samples taken from Ms. Parm. 3285 enabled the identification of pigments used for illuminations among those widely used during the medieval period in the creation of illuminated manuscripts [29–31]. Among these pigments, azurite blue seems to be related to the full-page illuminations at the beginning of the three chapters, while ultramarine blue seems to be used in the first letters of the paragraphs. These findings align with the fact that azurite was used more frequently than ultramarine, despite ultramarine being held in higher esteem, because of the much higher cost of this latter pigment.

However, a precise attribution is not possible because the samples were not collected directly on the illuminations but came from incoherent deposits. Thus, the use of ultramarine blue, perhaps in combination with azurite to save costs, in the full-page illuminations or at least in parts of them cannot be ruled out. To confirm this assumption, it would be necessary to carry on on-site non-destructive tests, such as portable X-ray fluorescence, directly on the manuscript, both on the fully illuminated pages and on the first letters of the paragraphs. Unfortunately, due to the preciousness of the work and the need to reduce handling operations to a minimum, at this moment, it was not possible to carry out these tests, which hopefully will be carried out in the future.

With the introduction of Prussian blue in 1704, azurite and ultramarine were displaced as the most commonly used blue pigments in Europe. This shift is also evident in this manuscript, where, in addition to azurite and ultramarine blue, the presence of Prussian blue pigment grains was also detected. In fact, over the centuries, the manuscript underwent numerous restoration interventions before the latest one. In particular, two recent interventions were probably carried out around the second half of the 19th century and later at the beginning of the 20th century, as reported in the archives of the Biblioteca Palatina library. During one of these interventions, the illuminations were probably retouched to renew the colors or to fill some lacks, using the Prussian blue pigment.

In conclusion, the analyses of the samples taken from this artwork allowed us to identify not only the pigments that were originally used for the creation of the illuminations, which, due to their preciousness, underline the importance of this manuscript since its production dating back over six hundred years, but also to confirm the execution of restorations over the time to preserve this beautiful work of art for future generations.

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