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The illuminated manuscript *Corale* 43 and its attribution to Beato Angelico: Non-invasive analysis by FORS, XRF and hyperspectral imaging techniques

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1. Introduction

In recent years, the approach to the study and preservation of the ancient librarian assets has significantly changed thanks to the introduction of scientific investigations in support of scholars' and art historians' research. In particular, in the study of illuminated manuscripts, the use of analytical techniques aimed at the identification of artists' materials, techniques and manufacturing processes has been acknowledged as highly profitable. Moreover, in some cases scientific investigations provided decisive results to solve open questions related to the historical and cultural context, textual interpretation and chronological collocation of the manuscript.

In the most general meaning of the definition, an illuminated manuscript is a handwritten book adorned (illuminated) with colorful and finely painted miniatures, decorations, letters and borders, added to the text to enrich and underline the contents and the value of the book [1]. Decorations and miniatures, skillfully placed in the handwritten page, resulted in a kind of lighting, luxurious effect. In several cases, along with its historical and textual value as part of the librarian heritage, an illuminated manuscript is a true work of art, with an inherent artistic value deserving dedicated studies and care. This circumstance is not rare for manuscripts produced during the Early Renaissance, when it was standard practice for famous artists and important painters to be entrusted as master illuminators [2].

The choice of materials and techniques used by artists depended on the geographical, cultural and historical context, and followed the secret recipes and the typical procedures of guilds and workshops entrusted with the manufacture of the book. Thus, the identification of constituent materials can help to shed light on different aspects – such as the manufacturing processes, dating and authorship of the book - which are often scarcely documented, or unknown. However, when dealing with ancient manuscripts, the plethora of analytical techniques usable for investigating polychrome artworks is highly reduced. In the majority of cases, sampling techniques are not allowed, except when small detached fragments are available, or if sophisticated ultra-microsampling methods are adopted [3]. Indeed, the typical dimensions of miniatures, comprising a high variety of pictorial materials and fine details in small sized areas, exclude the possibility of taking representative microsamples without compromising the integrity of the artwork. Moreover, sampling techniques, even when partially admitted, cannot be used extensively, thus preventing collection of statistically meaningful sets of data. In the last decade, important technological advancements in portability and affordability of devices for in-situ analysis fostered applications of non-invasive techniques to illuminated manuscripts: portable Micro-Raman spectroscopy, often combined with X-Ray Fluorescence (XRF), demonstrated to be effective in identification of pigment palettes in manuscripts [4–10]. Also Reflectance Spectroscopy in the Visible (Vis) and Near Infrared (NIR) regions has been successfully employed to investigate illuminated manuscripts. In particular, Vis-NIR reflectance spectroscopy, implemented in one- and two-dimensions (1D and 2D), that is as Fiber Optics Reflectance Spectroscopy (FORS) for spot analysis and as hyperspectral imaging spectroscopy (HSI) for areal investigations, was profitably used for identification and mapping of pigments and their mixtures [11–14]. As clearly emerges from the published literature, a suitable combination of complementary techniques is the most effective strategy to attain a comprehensive identification of pictorial materials.

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In the present work, a multi-analytical approach, based on the combination of non-invasive techniques implemented with portable and handy devices, has been adopted to carry out scientific investigations on a precious illuminated manuscript, the *Corale* 43, belonging to the collection of the Biblioteca Medicea Laurenziana in Florence. The manuscript is datable approximately to the first half of 15th century and still has uncertain attribution. Depending on the different hypothesis formulated by art historians, its attribution varies between Zanobi Strozzi (1412–1468), follower of Beato Angelico, also known as Fra Angelico (1395/1400–1455), the master Fra Angelico himself, and some other unknown illuminator of his circle [15–19].

Despite the art-historical interest and the high artistic value of *Corale* 43, this manuscript was never investigated by means of analytical techniques before the present work. This paper illustrates the results of scientific analysis performed for the first time on this manuscript. Vis-NIR FORS was coupled with XRF to identify pigments and their mixtures, whereas HSI was used to map the occurrence of selected pictorial materials on the surface. These data lead to the identification of the pigment palette, thus providing new insights on the manuscript.

Besides investigating the case study of *Corale* 43, this work aims at contributing to a broader research project focused on the artistic production of Fra Angelico and his circle. More precisely: in 2007–2008 the San Marco Museum in Florence dedicated a special exhibition to the eclectic figure of Fra Angelico, acknowledged not only as an excellent wall and panel painter, but also as a skilled illuminator. With the occasion of this exhibition, a systematic study on the Early Renaissance manuscripts produced in the Angelico's entourage was initiated. The first outcome of this project was the publication of scientific analysis carried out on one of the most significant items of the San Marco Museum collection, the *Graduale* 558, an illuminated manuscript of certain attribution to Fra Angelico, and dated to third decade of '400 [20]. The studies on *Graduale* 558, furtherly expanded in subsequent years, lead to accomplishing the characterization of the pictorial materials of this manuscript [21].

The present work, now dedicated to *Corale* 43, is the next step in the systematic analysis of artists' materials and techniques of the corpus of manuscripts produced in the Florentine area within the Angelico entourage. The new data acquired on *Corale* 43 have been compared with those previously gathered on *Graduale* 558 in order to highlight similarities and differences between the two illuminated books. Thus, new evidences to take into account the attribution problem of *Corale* 43 were provided, along with new insights on the 15th century illumination art of the Florentine area.

2. Materials and methods

2.1. The illuminated manuscript Corale 43

The *Corale* 43 (size 510 mm × 372 mm) is an antiphonal illuminated choirbook on parchment. It contains 261 folia, nine of which are illuminated with historiated initials and some of them with large and rich decorations and histories in the borders. The nine illustrated folia of the manuscript, classified as: f.1r, f.147r, f.168v, f.186r, f.199r, f.220r, f.241r, f.253r, f.256v, are shown in Fig. 1. Beside the nine folia illuminated with miniatures, the book contains several folia with minor decorations and pen-flourished letters.

Although *Corale* 43 is datable between the third and the fifth decades of the 15th century, a lack of documentation about its production makes it difficult to date it more precisely.

The only ascertained fact about *Corale* 43 is that it comes from the same place as *Graduale* 558, the convent of San Domenico di Fiesole near Florence, which was the venue of the community of the religious Dominican Order where Fra Angelico became friar, lived and worked. The manuscript is supposed to have remained in its original location for centuries, until the Napoleonic suppression of religious orders [22]. Subsequently, in 1809, it was moved to the Biblioteca Medicea Laurenziana in Florence, where it is still kept, available for public view. No other historical documentation is available on the genesis and history of *Corale* 43. The authorship of the manuscript remains debated.

The first studies on *Corale* 43, dated back to the beginning of the 20th century [15], acknowledged the manuscript as coming from Angelico's environment, and ascribed the miniatures to Zanobi Strozzi, one of the closest followers of Angelico. This attribution was accepted until 1995, when the art historian Boskovits reexamined the manuscript and confuted the previous attribution by ascribing the miniatures to the master Beato Angelico himself, with a dating around 1435–40. However, this proposal has not been accepted unanimously and it has also been suggested to maintain the authorship in the circle of Fra Angelico, perhaps to an unknown follower. Moreover, a possible compresence of different artistic hands was also suggested [16–19]. In fact, in the manuscript, in addition to the presence of a less skilled illuminator next to the main artist [17], some contradictory aspects emerged that challenged the notion of a complete autography of Fra Angelico.

On one hand, the originality of many iconographic inventions in the scenes depicted in the book reveals the genius of a great artist, thus suggesting Fra Angelico, whose wall paintings in the convent of San Marco are recalled in some scenes. Furthermore, it is not straightforward to attribute these illuminations to Zanobi Strozzi, who shows different characteristics in his later illuminated manuscripts. On the other hand, other arguments against an attribution to the master Beato Angelico can also be justified: for example, the miniatures in *Corale* 43 are much less refined with respect to the detailed scenes painted by Angelico in *Graduale* 558. Other differences among the two manuscripts stand out such as the palette, the choice of color combinations and the pictorial techniques. In *Corale* 43 figures and flesh tones appear finished with quick traits of superimposed and transparent colors, which reveal the lower drawings, a pictorial technique that is not observed in *Graduale* 558.

A comparison among the nine illuminated pages in *Corale* 43 makes it possible to observe stylistic differences and discrepancies in the quality of painting technique, thus suggesting the possibility of compresence of different hands in the same manuscript.

2.2. Analytical techniques

2.2.1. Fiber optics reflectance spectroscopy

FORS reflectance spectra were recorded in the Vis-NIR region using two Zeiss spectra-analyzers, MCS601 UV-NIR and MCS611 NIR 2.2 WR models, which were mounted on the same chassis together to a voltage-stabilized tungsten-halogen lamp (20 W, Model CLH600). Measurements were acquired in the 350–2200 nm range, with 0.8 nm/pixel (resolution: approximately 2 nm) and 6 nm/pixel (resolution: approximately 15 nm) acquisition steps for the 350–900 nm and 900–2200 nm ranges, respectively. An optical fiber bundle was used to illuminate the target and collect the reflected radiation. The bundle has one end split into three arms so as to be linked to the lamp and the two spectra-analyzers, while the other end is connected to a 8°/8° probe-head. The investigated spot had an almost circle-shaped area with a diameter of 2 mm. Calibration of the spectra-analyzer was performed by measuring a Spectralon® 99% diffuse reflectance standard.

The FORS measurements on *Corale* 43 were performed on 244 spot areas, selected according to the indications of art historians and curators, on the painted illustrations and selected decorations, including pen traits and inks.

The set analyzed included 14 folia: the nine illuminated folia (Fig. 1), and the additional folia: f.8r, f.38r, f.46r, f.71r, f.95r, including high-quality decorations and pen-flourished letters.

The acquired reflectance spectra were compared with reference data included in a FORS spectral library of pigments [23].

Fig. 1. *Corale* 43: the nine pages decorated with miniatures, classified as: f.1r, f.147r, f.168v (First row), f.186r, f.199r, f.220r (Second row), f.241r, f.253r, f.256v (Third row).

2.2.2. X-ray fluorescence

All measurements were carried out using a Bruker Tracer IIISD portable analyzer equipped with a rhodium anode, a palladium anticathode and a Peltier-cooled SDD detector capable of 145 eV resolution at 100,000 counts. The measuring spot is approximately 4 mm × 7 mm in size. The spectra were collected at 40 kV and 12 μA with a vacuum pump (0.01 Torr) for enhancing light element sensitivity and a count time of 180 s.

X-ray sources can easily penetrate parchment (or other light supports) collecting fluorescence signals from the back side of the folium under analysis and from one or more underlying folia, if written or painted areas are present. Taking this into account, XRF measurements were performed on spots without drawing or paint on the back side. In addition, to exclude contributions from painting on other folia, a PMMA (polymethylmethacrylate) slab (1 cm thick) was positioned below the page under investigation [24–26].

2.2.3. Hyperspectral imaging

A prototype of a new hyperspectral camera, Specim IQ - not commercially available at the time of this study - provided by SPECIM Spectral Imaging Ltd. (Oulu, Finland) to IFAC-CNR as a testing laboratory [27], was used to perform analysis on a subset of selected pages. The camera is very compact (207 mm × 91 mm × 126 mm) and lightweight (1.3 kg) and especially suitable to perform fast measurements, with a data recording time variable from ~0.6 s to 300 s, depending on the illumination level. The camera operates in the 400–1000 nm spectral range with

7 nm spectral resolution. To perform measurements the camera was mounted on a tripod, placed at a distance of about 50 cm from the target surface. The surface was illuminated using two Solux 50 W 36° MR16, 4700 K light sources, selected to ensure a minimum lighting impact on this highly photosensitive object. The two light sources were placed symmetrically with respect to the normal direction at the target surface.

The white reference calibration was performed before each session of measurements. It was made using a certified white reference Spectralon® 99% diffuse reflectance target, framed together with the scene to be examined.

Hyperspectral data were acquired on a subset of selected folia, due to practical constraints on acquiring images on all the illuminated pages. In the present paper the results obtained on f.186v are reported, as these are relevant to provide additional insight on the pictorial technique and materials used to depict the historiated scene. The data were elaborated using the ENVI® software package [28]. The Spectral Angle Mapping (SAM) method, a supervised classification algorithm, was used for hyperspectral data analysis. This method evaluates the similarity between each spectrum associated with the pixels of the imaged area and a reference spectrum (endmember) [29,30], by calculating the spectral angle between them. The use of SAM is effective to visualize pixels that have the same spectral behaviors in a false color map and it has been adopted here to distinguish pigment mixtures, similar in hue, that were used. The SAM method is insensitive to the spectral intensity, and therefore, it is recommended to treat data acquired in-field, especially in cases of non-ideal illumination conditions which causes undesired variations in the reflectance intensities.

3. Results and discussion

The primary aim of the non-invasive measurements campaign was the identification of the painting materials, the pigments and their mixtures, used to accomplish the different miniatures. In fact, at the preliminary visual inspection, the book featured an uncommon variety of hues and colors, another indicator of different hands in the making of the illuminations.

The FORS data acquired on the selected areas were combined with XRF measurements to provide a sufficiently exhaustive characterization of materials. However, to get a deeper insight on the artist's techniques, information about the distribution of a given pictorial material over an extended painted area may be important. Thus, hyperspectral imaging was used to map the distributions of selected pigments of interests.

3.1. Parchment and gilding

The folia constituting the manuscript are made of parchment. It is known that, according to the ancient recipes, the folia for illuminations were pre-treated, for example using calcium carbonate or finely powdered bones, in order to smooth the surface and make a basis for painting or writing with inks [31].

A FORS spectrum of an unpainted area has been acquired in each investigated folium, in order to ascertain if some absorption band of the support could affect the spectra acquired on colored areas. All the spectra acquired on the unpainted parchment showed similar characteristics, and a typical example is reported in Fig. 2. As expected, in the visible region no spectral features attributable to the support are present. In the NIR region, the absorption bands due to water molecules and parchment are recognizable. The broad absorption bands center at approximately 1200 nm, 1500 nm, 1750 nm, 1900–2000 nm are due to overtones and combination bands of the fundamental vibrational modes of hydroxide and water.

As reported in [32], the absorption features due to the methyl and methylene groups of the parchment are found in the same wavelength intervals of water and hydroxide. The absorption peaks at around 1730 nm and 1690 nm can be assigned to the first overtones of the symmetric and asymmetric stretching fundamental modes of CH_2 and CH_3 groups.

XRF spectra on two unpainted parchment spots revealed the presence of following elements: Ca and Fe as minor components and K in trace amount. The fact that Ca occurred as major component, and that it was found as ubiquitous element in all the acquired XRF spectra, strongly suggests that its presence is due to some pre-treatment of the parchment. In addition, since no substantial counts of P were detected by XRF, the use of calcium carbonate for pre-treating the parchment appeared as the most likely candidate.

The gold leaves, which were extensively used in the *Corale* 43 for background and aureole areas, were made with gold. XRF could not be used to measure directly aureoles, due to their reduced dimensions. Au traces were detected by XRF in areas close to gilded details, such as aureoles. Moreover, the presence of gold was confirmed by the FORS spectra.

FORS data were also acquired in areas where the gold layer appeared detached or lacking, in order to study the preparation layer under the gold leaf. It was found that gypsum was present as a preparatory layer for the application of the gold leaves in mixture with iron(III) oxide

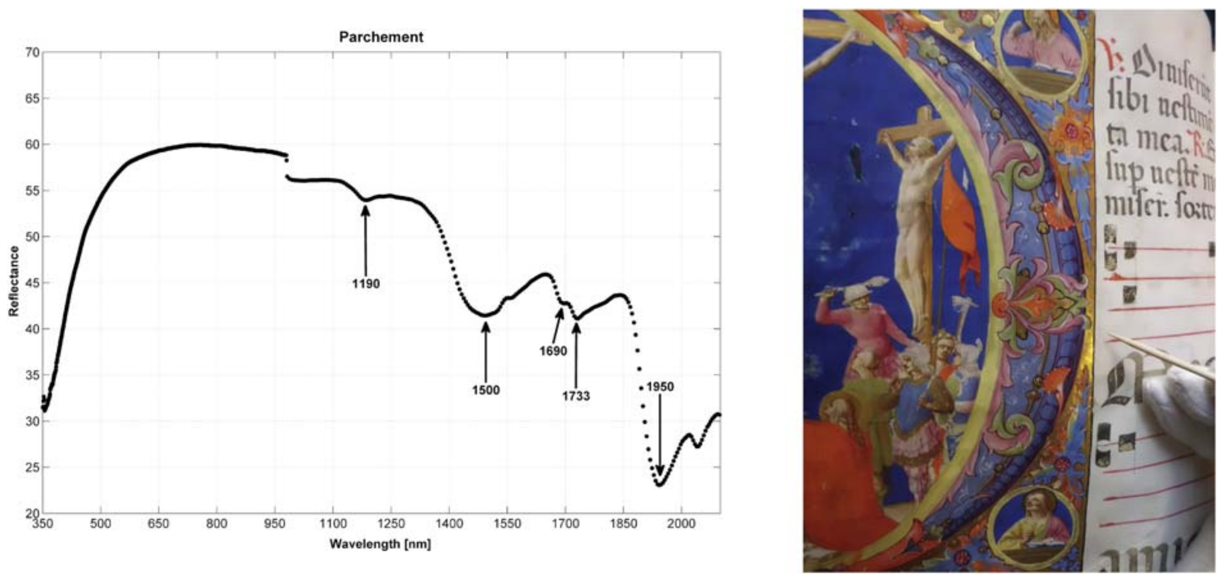

Fig. 2. The Vis-NIR reflectance spectrum (Left) of the parchment acquired on an unpainted area (Right) of the f.168v.

based pigments and aluminosilicate minerals, thus indicating a manufacturing process based also on use of bolo as background for gold application. FORS spectra, indeed, presented the typical features in the NIR of gypsum, calcium sulfate bi-hydrated ($CaSO_4 \cdot 2H_2O$). Gypsum FORS spectrum shows a characteristic triplet, constituted of three absorption sub-bands at 1450 nm, 1490 nm, 1535 nm, due to the first overtones of the OH-stretching of the lattice water, plus other water combination bands at approximately 1200 nm, 1750 nm and 1945 nm.

3.2. The palette

Corale 43 shows an interesting and nice variety of hues, including blue, blue-grey, pink, deep pink, red-orange, green, yellow, with particular combinations such as blue-pink-green; grey-violet-deep pink-green, blue-yellow, red-yellow, and red-green-yellow. The colors are usually very intense and vivid, except green shades, which appear pale, dull and predominantly with a particular yellowish tone.

Those hues were obtained with a traditional palette, which was defined, mainly, by using FORS with the support of XRF. In Table 1 an overall view of all the materials identified, with their collocation in the examined folia, is given.

After identification of main pigments and their mixtures, the study of constituent materials was focused in particular on blue and green areas. These were indeed indicated by art historians as deserving deeper investigations to shed light on the similarities and differences with the other analyzed manuscript, the *Graduale* 558, coming from the same convent as *Corale* 43.

3.2.1. Blue and bluish areas

Natural ultramarine blue (a pigment obtained from the semi-precious stone lapis lazuli) and azurite were the two blue pigments detected in the manuscript. They are both easily identifiable using FORS, due to their characteristic Vis-NIR reflectance spectra.

A set of 86 spectra was acquired on blue and bluish areas selected throughout the nine illuminated folia of the book. The data acquired were interpreted and identified by comparison with reference spectra of pure pigments from the IFAC-CNR spectral archive.

The numerous data acquired on blue areas indicated that, in *Corale* 43, the precious natural ultramarine blue was the most extensively used. This pigment was detected in most of blue and bluish areas, including background areas like the sky and the ornamental elements of the initials, and it was not dedicated, as it could be expected, to only depict the most important and representative holy figures.

As an example, Fig. 3 shows the spots selected on two visibly different blue areas of the lower scene in f.1r (points P12 and P13) and their FORS spectra, reported along with the reflectance spectrum of a pure lapis powder laboratory reference. The color of natural ultramarine blue is due to charge transfer electronic transitions inside the S^{3-} group that is present in the lattice of the complex aluminum-silicate [33–34]. These transitions are responsible for the typical Vis-NIR spectrum of pure ultramarine blue (Fig. 3), characterized by a typical strong

Table 1
Pigments and dyes identified.

	Blue	Green	Yellow	Brown	Red	Pink & purple	Flesh tone
f.1r	Ultramarine blue	Azurite + lead tin yellow	Lead-tin yellow	Iron earth pigments	Red lake	Red lake	Lead white, iron earth pigments
	Azurite	Ultramarine blue + lead tin yellow			Red lead		
					Red earth		
f.8r	Ultramarine blue	Malachite	Lead-tin yellow		Vermilion		
f.38rn	Ultramarine blue		Lead-tin yellow		Vermilion		
f.46r	Azurite	Green earth	Lead-tin yellow		Red lake		
					Red earth		
f.71r	Ultramarine blue	Azurite + lead tin yellow				Red lake + ultramarine blue	
	Azurite	Ultramarine blue + lead tin yellow					
f.95r	Ultramarine blue				Vermilion	Red lake + ultramarine blue	
	Azurite						
f.147r	Ultramarine blue	Azurite + lead tin yellow	Lead-tin yellow	Iron earth pigments	Red lake	Red lake	Lead white, iron earth pigments
	Azurite		Yellow earth		Red lead		
					Red earth		
					Vermilion		
f.168v	Ultramarine blue	Ultramarine blue + lead tin yellow	Lead-tin yellow		Red lake	Red lake	Lead white, iron earth pigments
	Azurite		Yellow earth		Red lead		
f.186v	Ultramarine blue	Ultramarine blue + lead tin yellow	Lead-tin yellow		Red lead	Red lake	Lead white, iron earth pigments
	Azurite	Azurite + lead tin yellow			Vermilion		
f.199r	Ultramarine blue	Ultramarine blue + lead tin yellow	Lead-tin yellow	Iron earth pigments	Red lake		Lead white, iron earth pigments
	Azurite		Yellow earth		Red lead		
					Vermilion		
f.220r	Ultramarine blue	Ultramarine blue + lead tin yellow		Iron earth pigments	Red lake	Red lake + ultramarine blue	Lead white, iron earth pigments
	Azurite				Red lead		
f.241r	Ultramarine blue	Ultramarine blue + lead tin yellow	Lead-tin yellow		Red lake	Red lake + ultramarine blue	
		Azurite + lead tin yellow	Yellow earth		Red lead		
					Red earth		
					Vermilion		
f.253r	Ultramarine blue					Red lake + ultramarine blue	
	Azurite					Cinnabar + iron earth pigments	

absorption band centered around 600 nm, and without any other characteristic spectral feature in the NIR region [35]. The comparison of the ultramarine blue reference spectrum with the FORS data acquired in P12 and P13 clearly shows that both these spectra perfectly correspond to a pure natural ultramarine blue pigment laid on the parchment support. Apart from the spectral features of the parchment, no other bands besides those of lapis lazuli are present. This excludes, for these areas, the use of mixtures of pigments (e.g. addition of white lead) to obtain the paler hue of background.

Moreover, XRF data acquired on P13 evidenced the following elements: Ca, K, Si, S (main elements), Al (minor element) and Fe (traces), which are consistent with the presence of natural ultramarine blue without being mixed with lead white or other pigments.

The second blue pigment was azurite, used less abundantly than natural ultramarine blue, but nevertheless detected throughout all the illuminations of *Corale* 43. It seems that the azurite has been used in preference to paint garments and vests. In Fig. 4, as an example, the upper scene of f1.r with the indication of the measured point (P1) on the vest of Jesus is shown. Fig. 4 also reports the FORS spectrum acquired in P1 compared with the reference spectrum of pure azurite and the spectrum of the parchment.

Azurite is a basic copper(II) carbonate and its color is given by the electronic *d-d* transition of the copper(II) [35–36]. As shown in Fig. 4, its Vis-NIR spectrum shows a reflectance peak at about 450–480 nm and a broad absorption band in the 600–900 nm range. In the NIR region the pure pigment shows a diagnostic absorption band at about 1500 nm, as well as another typical spectral feature in the 2200–2400 nm region. The configuration adopted for FORS measurement did not make possible detection of signals above 2200 nm. However, the diagnostic band at 1500 nm, as well as the spectral shape in the 400–900 nm region, clearly indicate that the FORS spectrum acquired on the mantle of Christ (P1) can be unambiguously identified as azurite. This result has also been confirmed by XRF, which revealed on the same area a significant presence of Cu with Fe, and traces of Ca, P, and Si.

In other cases the FORS spectra of blue and bluish areas presented peculiar spectral characteristics, which indicated a use of mixtures of blue pigments with some other pigments. This was the case of the blue areas in the historiated initial ‘S’ letter of f.186r. Here, as reported by Dillon Bussi [17], the blue sky was anomalously found of flatness appearance under stylistic visual inspection. This stylistic evidence might be related to the work of a possible collaborator of the main artist [17]. In order to better investigate this aspect, several FORS spectra were acquired on the blue areas of f.186r and then comparatively evaluated. In Fig. 5 the FORS spots measured are shown, and the spectra of two spots, P1 and P4, corresponding to different hues of blue, are reported along with the reference spectrum of pure natural ultramarine blue.

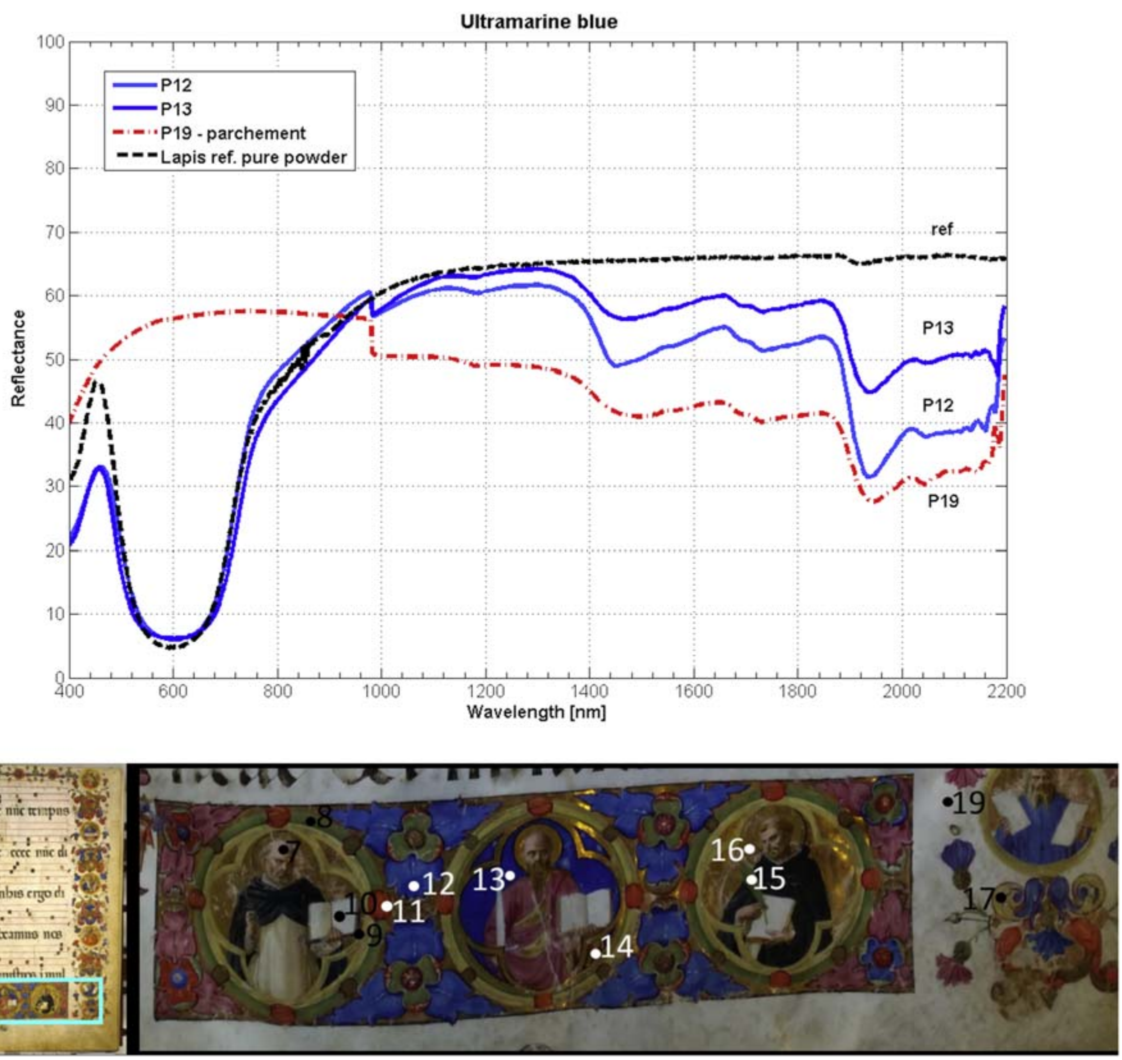

Fig. 3. (Top) Vis-NIR reflectance spectra acquired by FORS in P12 and P13 of f.1r, corresponding to lighter and darker blue areas, compared with the reference spectrum (ref) of powder of pure lapis lazuli (natural ultramarine blue) and with the unpainted support (P19). (Bottom) Detail of f.1r with the position of the measured spectra. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

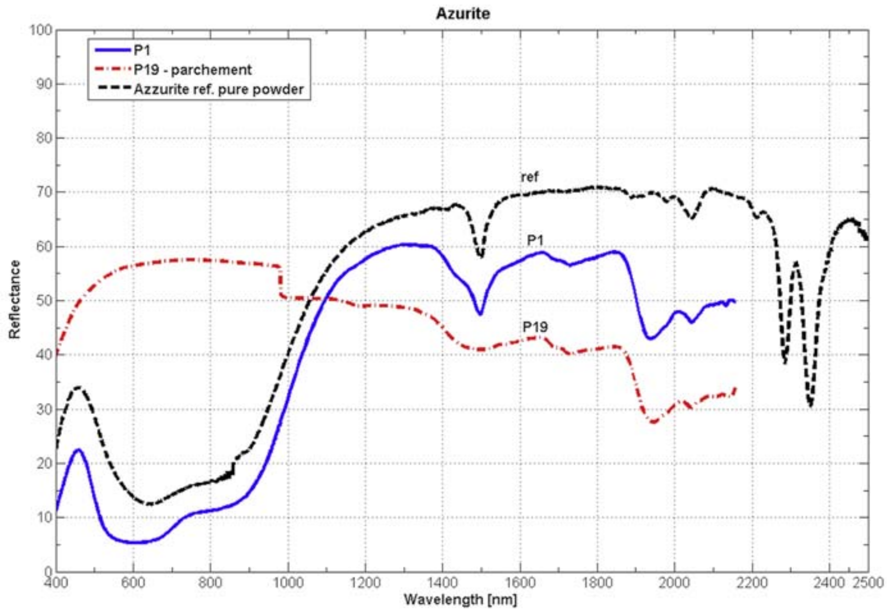

Fig. 4. (Top) Vis-NIR reflectance spectra acquired by FORS on the mantle of Christ (P1) in the illuminated letter of f.1r. Comparison with the spectrum a reference azurite (ref) and with the unpainted support (P19). (Bottom) Detail of f.1r with the position of the measured spectra.

The typical absorption band centered at 600 nm indicates that both the P1 and P4 spectra contain ultramarine blue. However, the P1 and P4 spectral behaviors in the 500–600 nm region differ from each other, suggesting that the P4 spectrum is not a pure ultramarine blue, but was likely obtained as mixture of ultramarine with red lake. The presence of red lake was hypothesized on the basis of the shape of the absorption band around 530–560 nm, featuring two weak shoulders in that spectral range. The presence of a red pigment in these spots is also confirmed by the slightly violet appearance of this bluish area.

In order to extend the spot size information to larger areas and to visualize the distribution of those mixtures/hues on the overall illuminated scene, hyperspectral imaging was used. A selected ROI (Region of Interest), as reported in Fig. 6, was imaged using the hyperspectral camera and the corresponding data cube was acquired [27].

The SAM classification algorithm was used to process the hyperspectral data in the selected area. The two reflectance spectra extracted from the data cube in correspondence of points P1 and P4 (Fig. 5), respectively, were used as endmembers for SAM classification. The result obtained is reported in the false color map of Fig. 6, where the P1 spectrum is mapped as blue and the P4 spectrum is mapped as green-light. This map indicates that the mixture used in P4, was also used to make all blue details, excluding the sky and the vest of the central figure, which didn't result classified in this map, since it was decorated with pure azurite, as revealed by the FORS data (P22).

3.2.2. Green areas: similarities and differences with the Graduale 558

Generally speaking, the identification of the greens palette in illuminated manuscripts is always a challenging task, because of the high variety of possible pigments, pure or mixed, used by illuminators over the centuries to obtain the several shades and hues of green [37–38]. Indeed, green hues and shades were made not only with green pigments, but also by mixing blue and yellow pigments. This choice could depend

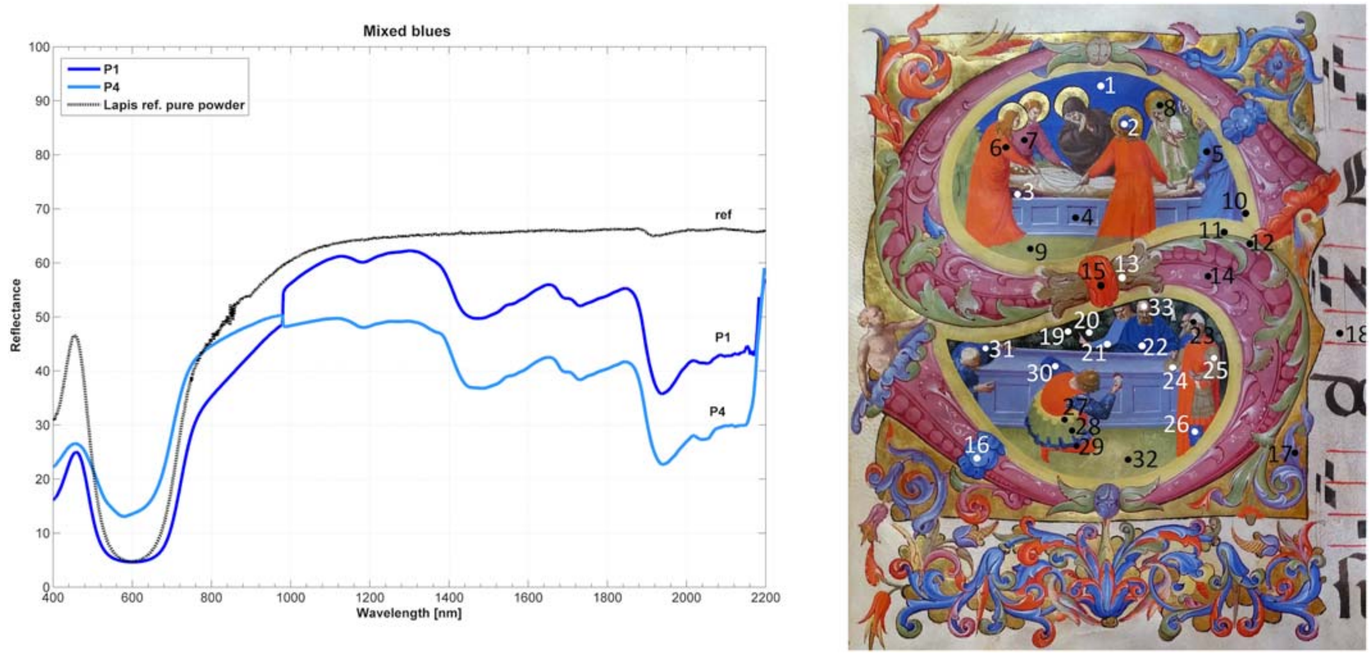

Fig. 5. (Left) Vis-NIR reflectance spectra acquired by FORS on the sky (P1) and on the bluish area (P4) of f.186r, compared with the reference spectrum (ref) of powder of pure lapis lazuli (natural ultramarine blue). (Right) Detail of the illumination in f.186r with the position of the measured spectra. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

on several factors, such as the artist's intention, the typical recipes and techniques of the illumination workshops, and the local availability of materials. Also in the case of *Corale* 43 the study of green areas had a particular interest for the historical contextualization of the manuscript.

A set of 40 FORS spectra was acquired on green areas featuring different hues and intensities according to the visual inspection. The majority of the spectra recorded showed similar spectral features which indicated a predominant use of mixtures between yellow and blue pigments. As an example, the Vis-NIR spectra acquired on two different greens (P11 and P12) selected in f.147r are reported in Fig. 7. Around 500 nm, both reflectance curves rise, indicating the presence of a yellow pigment. Two residual weak absorption bands centered around 630 nm and 840 nm are attributable to a blue pigment, which can be clearly identified as azurite in the case of point P12, as indicated by the weak, yet detectable, absorption band at 1500 nm. The different behavior observed in P11, in principle, could be explained with the presence of another blue pigment (natural ultramarine blue) or, alternatively, with a very low amount of azurite in the mixture. Vis-NIR FORS spectra are not very diagnostic in the identification of some of the traditional yellow pigments, such as lead-tin yellow and Naples yellow, for instance. Therefore, XRF was used to corroborate the identification of these mixtures. In Fig. 8 the XRF spectra acquired in the same areas on f.147r, P11 and P12, are reported. A noticeable presence of Pb was detected in both the spots, as well as presence of Sn, thus supporting that lead-tin yellow was the pigment used in both the mixtures. In addition, the presence of Cu, detected in both the areas,

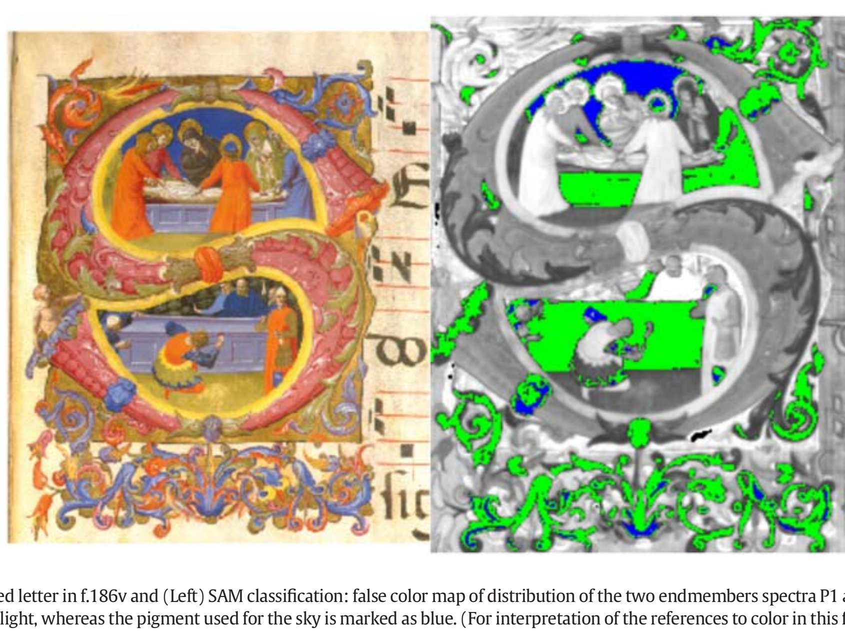

Fig. 6. (Left) Detail of the illuminated letter in f.186v and (Left) SAM classification: false color map of distribution of the two endmembers spectra P1 and P4. The pigment mixture used for the coffin (P4) is mapped as green-light, whereas the pigment used for the sky is marked as blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

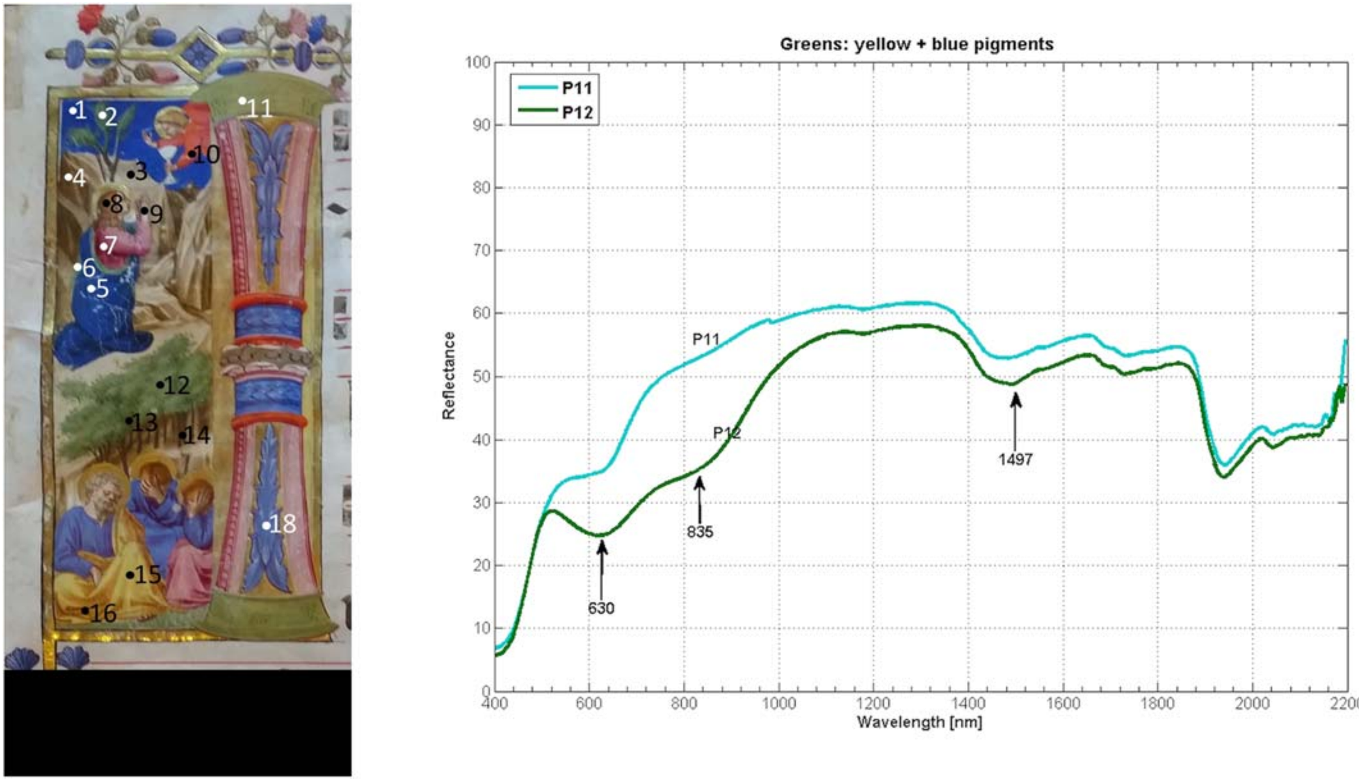

Fig. 7. (Left) Detail of the illumination in f.147r and the position of measured spectra. (Right) Vis-NIR reflectance spectra acquired by FORS on the green of the capital letter "I" (P11) and on the foliage (P12) of f.147r. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

but with a higher number of counts in P12, confirmed the hypothesis of use of azurite at different concentration rates in the two mixtures.

The analysis of the 40 spectra with green hues showed that, besides mixtures between blue and yellow pigments in different concentrations, also pure green pigments were used in the manuscript. In particular, malachite and green earth were detected, although used to a lesser extent. This fact can be clearly observed in Fig. 9, showing the overall view of all the FORS spectra acquired on green areas: few reflectance spectra in the group showed a different spectral behavior, not identifiable as mixture of blue and yellow, but typical of pure green pigments. Thus, the subset of 40 spectra was processed with a statistical approach, in order to gain some insights on the distribution of different greens throughout the manuscript. Principal Component Analysis (PCA) was applied to the spectral data, after a pre-treatment of the spectra encompassing a smoothing process (Sawitzky-Golay method). The analysis was limited to the spectral sub-range 400–1000 nm. The PC1–PC4 score plot reported in Fig. 10 clearly shows a main group of data, associated with the spectra for greens obtained as mixtures, and a separate cluster, which includes the few spectra associated to pure greens pigments. The attribution of these data to the corresponding spots where they were acquired highlighted that these pure pigments were found exclusively on minor decorations and pen-flourished letters, but not in illuminated scenes. Therefore, these results indicate that only green colors obtained by mixing blue and yellow pigments were used for depicting the illuminations. This finding is an important element of difference with the manuscript *Graduale* 558, where, conversely, only pure green pigments, such as malachite and green earth, were found in the examined illuminations.

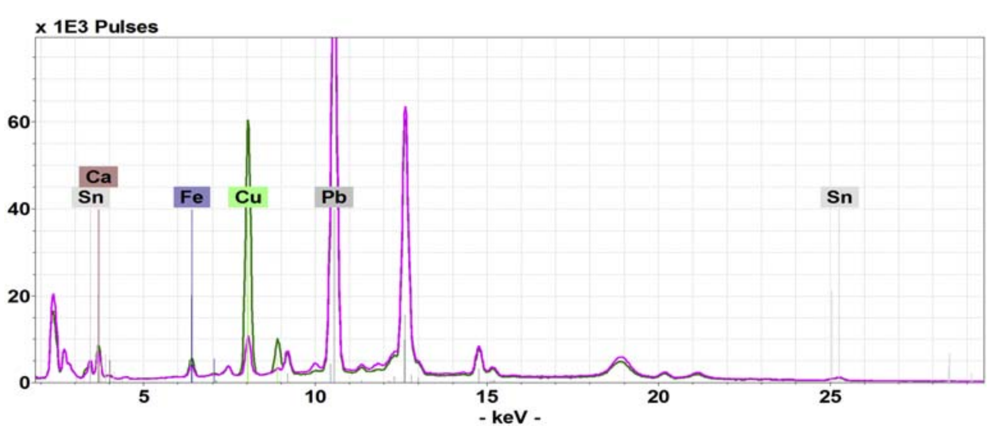

Fig. 8. XRF spectra of P11 (light green of the letter, pink line) and P12 (foliage, green line). Only K and L lines are marked. The Lα line of Lead is out of scale for a better reading of the spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

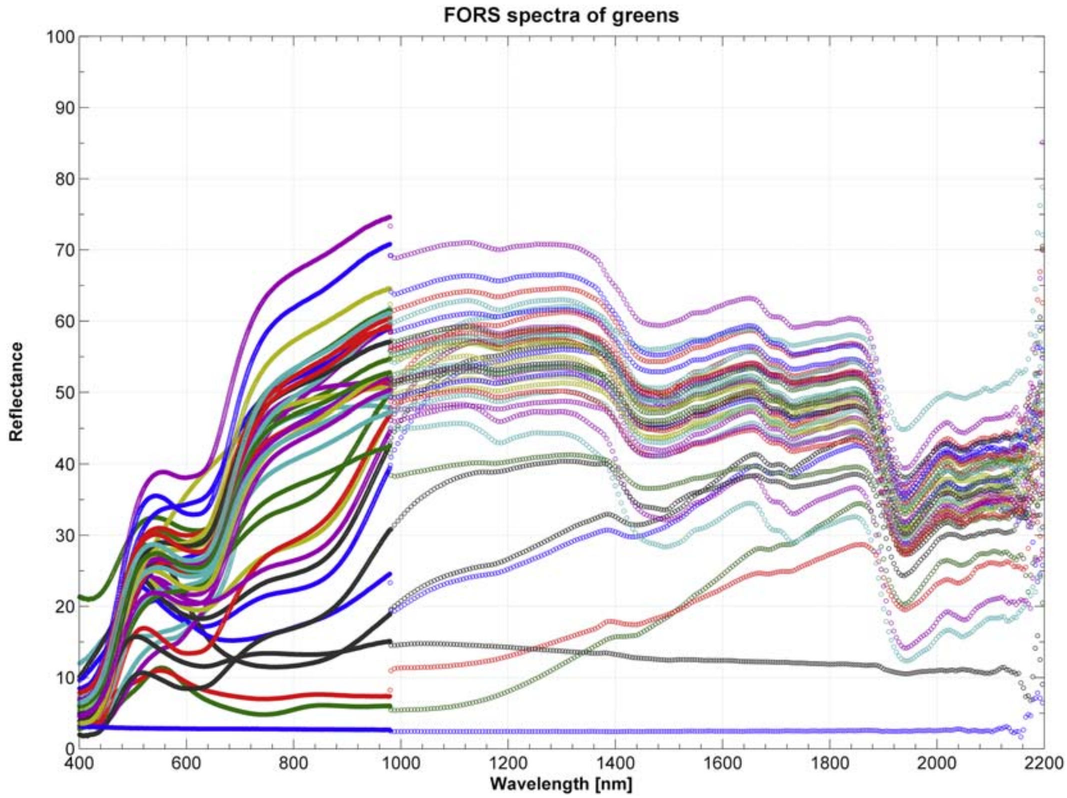

Fig. 9. The 40 FORS spectra acquired on all the green spots selected on *Corale* 43. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Summary of the analysis

The set of materials identified consist of a limited range of basic pigments, skillfully used, pure and mixed, in order to obtain a rich and colorful palette, accordingly with the habits of the Florentine circle of Fra Angelico.

Specifically, the FORS measurements on blue areas revealed the presence of two blue pigments, natural ultramarine blue (lapis lazuli) and azurite, with a prevalent use of the former over azurite. Ultramarine blue was also detected in mixture with red pigments, mainly red lake, at different concentrations to depict deep pink-violet-purple details.

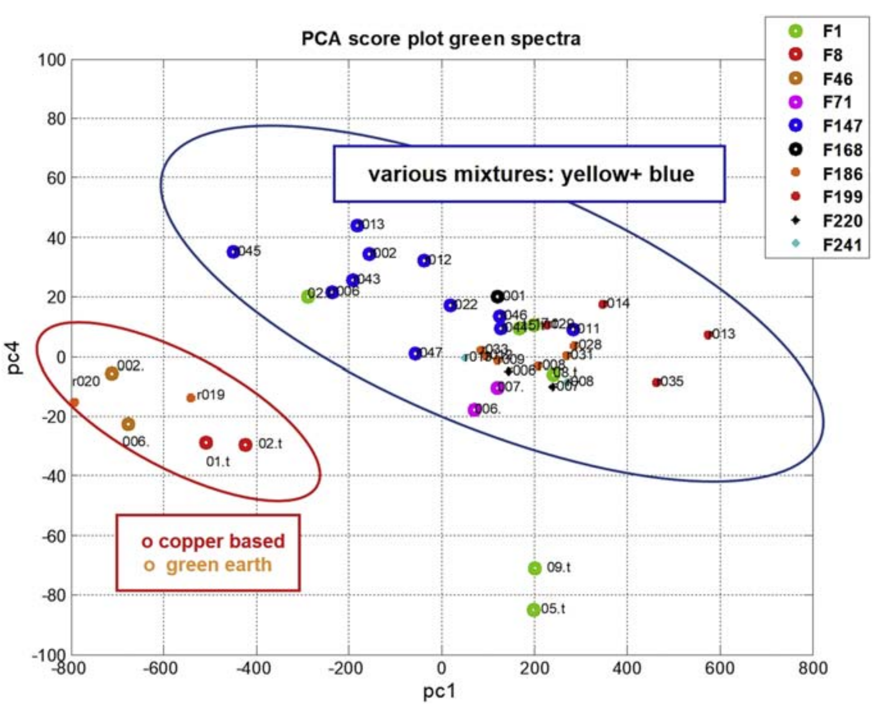

Fig. 10. PC1-PC4 score plot from the PCA data analysis applied to the set of the 40 FORS spectra acquired on green zones. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Azurite was prevalently used to depict the garments, including the mantles of holy figures, such as for the Christ mantle in f.1r. This is an element of difference with respect to the *Graduale* 558, in which all the analyzed blues areas resulted painted with ultramarine blue.

XRF combined with FORS allowed the identification of the yellows palette, which included essentially lead-tin yellow, used in lighter areas, and iron(III) hydroxide and oxide based pigments (yellow and brown ochre, natural and/or burnt earth pigments) used for darker and less saturated hues. In particular, the pigment lead-tin yellow was identified by the joint presence of lead and tin in the XRF spectra, as well as from its reflectance spectral shape (FORS). The ochre and earth pigments showed typical FORS spectra, in which the characteristic absorption bands of iron(III) are easily identified.

An accurate study of green areas demonstrated that almost all greens used in miniatures were obtained as mixtures of a yellow and a blue pigment, by varying their respective concentrations to obtain different shades and hues. Depending on the area considered, the greens were obtained using lapis lazuli or azurite, mixed with a lead tin-yellow, as indicated by the tin detected with XRF. Pure green pigments were never detected in illuminations. Only a sporadic presence of a copper-based green pigment, such as malachite, was revealed in pen flourished letters and side decorations, but not in painted parts attributable to the illuminator's work. This predominant use of mixed greens was considered a key information about this manuscript, since in the *Graduale* 558 Beato Angelico used only malachite to create the green and greenish shades. This is significant since it highlights another difference in the palettes of the two manuscripts.

As for the reds, different shades and hues, ranging from intense reds to purples and brown tones, occur in *Corale* 43. Fig. 11 shows the FORS spectra acquired on three red and reddish areas (P7, P10 and P26, respectively) in f.147v, representative of the typical reds observed throughout the pages of *Corale* 43.

The spectrum acquired in P7 is easily identifiable as a red-lake based pigment (likely extracted from an insect), based on the presence of the typical two weak bands at about 525 nm and 565 nm, along with the sharp increase of the reflectance in the 610–670 nm region. This identification is totally consistent with the rose-purple appearance of the color.

The spectrum acquired in P10, appears as an intense and saturated red and is characterized by a S-shape behavior. The inflection point of the spectrum positioned at approximately 565 nm is typical of red lead (minium). The presence of red lead was confirmed by XRF where only lead was found. Furthermore, XRF data acquired on red areas indicated a predominant use of vermilion based on the detection of mercury, typically associated with this pigment. XRF data also highlighted that in other cases other red areas were painted with both red lead and vermilion.

The third type of red pigment found in *Corale* 43 is exemplified by the FORS spectrum acquired in P26, which shows the typical behavior of an iron-oxide based red pigment, identifiable from the absorption band centered at 850 nm and the strong absorption below 550 nm.

Lead white was extensively detected throughout the book, especially in mixtures with other pigments. The presence of this pigment was detected by XRF and confirmed by the FORS spectra.

Black areas were depicted with carbon-based pigments, such as lamp black, bone black or vine black. The text and the musical notes were made by using an iron gall ink, apart from a case in which a note in the illuminated area of the f.220r was obtained with a carbon based pigment [27].

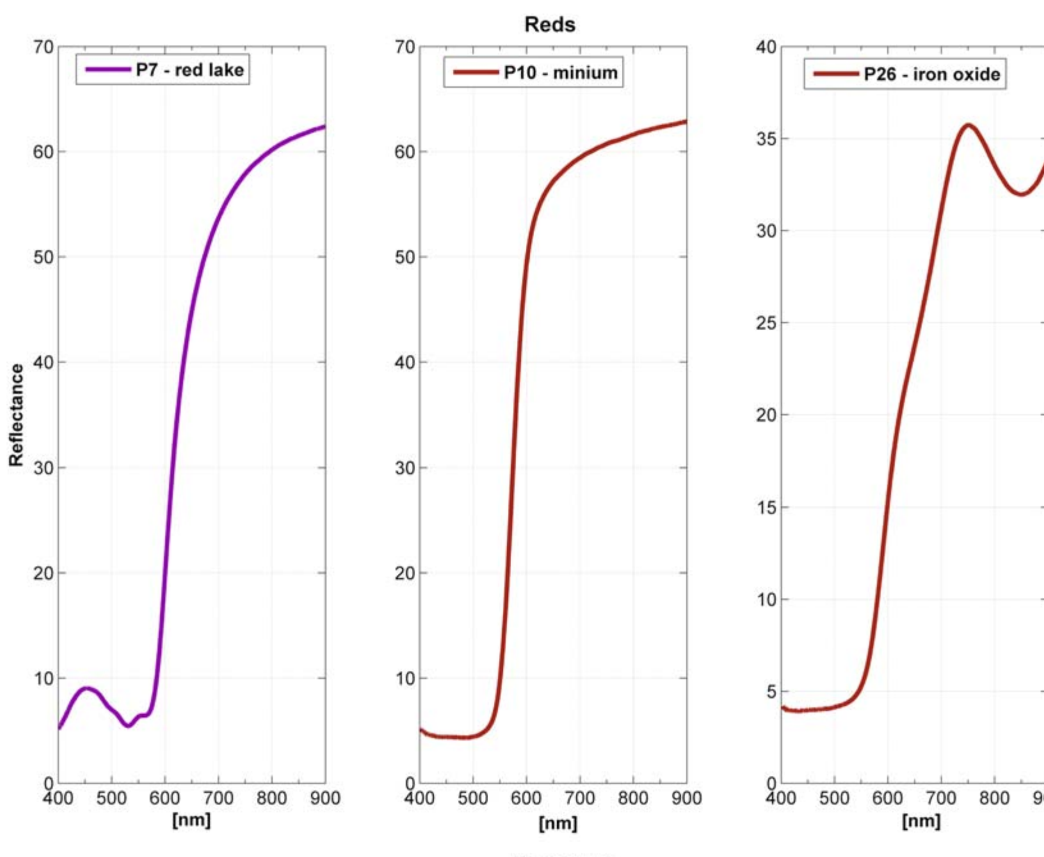

Fig. 11. Vis-NIR reflectance spectra acquired by FORS on three red areas in f.147v. a) P7 red-lake b) Minium c) Iron oxide. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5. Conclusions

In the study of illuminated manuscripts, besides the identification of pigments and constituent materials, every additional element about the manufacturing process, the artist's technique and the stylistic peculiarities may be precious in providing deeper insight on unknown elements such as authorship, dating, and historical contextualization.

In the present work, the combined use of Vis-NIR reflectance spectroscopy implemented in two versions, as spot-analysis (FORS) and as 2D hyperspectral imaging, together with portable XRF, demonstrated to be a powerful experimental methodology to achieve a deeper knowledge of the case study examined, the illuminated manuscript *Corale* 43.

Thanks to their non-invasive nature and fast data acquisition, FORS and XRF were extensively applied on all the illuminations of the manuscript, and on other significant decorated parts, to obtain a copious dataset, statistically meaningful, exploitable to reconstruct the wide gamma of pigments used and the palette. Subsequently, the additional use of a prototype hyperspectral camera provided 2D Vis-NIR hyperspectral data of selected scenes, which were processed using classification algorithms (SAM) to map the distributions of given pigment mixtures over selected areas. These maps proved to be effective to easily visualize where and to what extent a given material or a mixture was applied. Specifically, hyperspectral imaging highlighted a singular use of a blue mixture in selected scenes, such as in the illumination in f.147r. This result indicated that mapping and classification algorithms applied to hyperspectral data proved a practical means to highlight the presence of differently painted areas, or anomalies in the materials compositions.

The experimental protocol adopted, based on integrated use of spot-analysis and hyperspectral imaging techniques, proved to be very effective to attain exhaustive information in the study of illuminated manuscripts, especially when comparative analysis between different folia and or different books are required. Specifically, the results obtained on *Corale* 43 helped to confidently distinguish several objective differences between the palette of this manuscript and that one characterizing the Angelico's book *Graduale* 558. Namely, it was demonstrated that greenish hues in the illuminations of *Corale* 43 were always obtained as mixtures between blue and yellow pigments, whereas in *Graduale* 558 only pure copper-based green pigments were detected. Another difference was found in blue pigments. Two blue pigments, natural ultramarine blue and azurite were revealed in *Corale* 43. This characteristic use of blues did not correspond to the results obtained on *Graduale* 558, where only pure natural ultramarine blue pigment was identified. These evidences point to unbiased results identifying differences in the set of artists' materials used for the two manuscripts. It can be stated that part of the pigment mixtures detected in *Corale* 43 were not found in *Graduale* 558, where a preference for the use of pure pigments was observed resulting in a narrower palette of vivid colors.

Although these findings are not sufficient to draw conclusions, they cannot be neglected in a subsequent reexamination of attribution and dating questions. The obtained data foster further studies on other coeval manuscripts produced in the same area, with the challenging task of compiling an atlas of pigments and artist materials associated to the manuscripts corpus produced within the Florentine circle of the Angelico's followers.

References

[1] C. De Hamel, The British Library Guide to Manuscript Illumination: History and Techniques, University of Toronto Press, Toronto, 2001.
[2] Laurence B. Kanter, Painting and Illumination in Early Renaissance Florence, 1300–1450, Metropolitan museum of art, 1994.
[3] W. Devos, L. Moens, A. von Bohlen, R. Klockenkämper, Ultra-microanalysis of inorganic pigments on painted objects by total reflection X-ray fluorescence analysis, Stud. Conserv. 40 (3) (1995) 153–162.
[4] S. Pessanha, M. Manso, M.L. Carvalho, Application of spectroscopic techniques to the study of illuminated manuscripts: a survey, Spectrochim. Acta B At. Spectrosc. 71 (2012) 54–61.
[5] MINIARE, Manuscript Illumination: Non-Invasive Analysis, Research and Expertise, http://www.miniare.org 2013, Accessed date: 18 July 2017.
[6] L. Burgio, D.A. Ciomartan, J.H.C. Robin, Pigment identification on medieval manuscripts, paintings and other artefacts by Raman microscopy: applications to the study of three German manuscripts, J. Mol. Struct. 405 (1) (1997) 1–11.
[7] P. Vandenabeele, B. Wehling, L. Moens, B. Dekeyzer, B. Cardon, A. von Bohlen, R. Klockenkämper, Pigment investigation of a late-medieval manuscript with total reflection X-ray fluorescence and micro-Raman spectroscopy, Analyst 124 (2) (1999) 169–172.
[8] D. Bersani, P.P. Lottici, F. Vignali, G. Zanichelli, A study of medieval illuminated manuscripts by means of portable Raman equipments, J. Raman Spectrosc. 37 (2006) 1012–1018, https://doi.org/10.1002/jrs.1593.
[9] G. Van der Snickt, W. De Nolf, B. Vekemans, K. Janssens, μ-XRF/μ-RS vs. SR μ-XRD for pigment identification in illuminated manuscripts, Appl. Phys. A Mater. Sci. Process. 92 (1) (2008) 59–68.
[10] S. Mosca, T. Frizzi, M. Pontone, R. Alberti, L. Bombelli, V. Capogrosso, A. Nevin, G. Valentini, D. Comelli, Identification of pigments in different layers of illuminated manuscripts by X-ray fluorescence mapping and Raman spectroscopy, Microchem. J. 124 (2016) 775–784.
[11] P. Ricciardi, J.K. Delaney, M. Facini, J.G. Zeibel, M. Picollo, S. Lomax, M. Loew, Near infrared reflectance imaging spectroscopy to map paint binders in situ on illuminated manuscripts, Angew. Chem. Int. Ed. 51 (23) (2012) 5607–5610.
[12] J.K. Delaney, P. Ricciardi, L.D. Glinsman, M. Facini, M. Thoury, M. Palmer, E.R. de la Rie, Use of imaging spectroscopy, fiber optic reflectance spectroscopy, and X-ray fluorescence to map and identify pigments in illuminated manuscripts, Stud. Conserv. 59 (2) (2014) 91–101.
[13] C. Cucci, J.K. Delaney, M. Picollo, Reflectance hyperspectral imaging for investigation of works of art: old master paintings and illuminated manuscripts, Acc. Chem. Res. 49 (10) (2016) 2070–2079.
[14] M. Aceto, A. Agostino, G. Fenoglio, A. Idone, M. Gulmini, M. Picollo, P. Ricciardi, J.K. Delaney, Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry, Anal. Methods 6 (5) (2014) 1488–1500.
[15] P. D'Ancona, La miniatura fiorentina (secoli XI-XVI), 2 vols, Leo S, Olschki, Firenze, 1914.
[16] M. Boskovits, Attorno al "Tondo Cook": precisazioni sul Beato Angelico, su Filippo Lippi e altri, Mitteilungen des Kunsthistorisches Institutes in Florenz, XXXIX 1995, pp. 32–68.
[17] A. Dillon Bussi, Antifonario per il Proprio del tempo (dalla prima domenica di Quaresima al sabato), in: A. Di Lorenzo (Ed.), Omaggio a Beato Angelico. Un dipinto per il Museo Poldi Pezzoli, Catalog of the exhibition in Milan, 20 September – 2 December 2001, Cinisello Balsamo 2001, pp. 30–35.
[18] A. Dillon Bussi, scheda Cat. I. 32, in: M. Scudieri, G. Rasario (Eds.),Miniatura del 400 a San Marco. Dalle suggestioni avignonesi all'ambiente dell'Angelico, Catalog of the exhibition in Florence, San Marco Museum, 1 April – 30 June 2003, Firenze 2003, pp. 160–161.
[19] L. Kanter, Zanobi Strozzi miniatore e Battista di Biagio Sanguigni, Arte cristiana, 90, 2002, pp. 321–331.
[20] M. Bacci, M. Picollo, B. Radicati, A. Aldrovandi, A. Migliori, Studio dei materiali pittorici del Graduale 558 mediante tecniche spettroscopiche non invasive, in: M. Scudieri, S. Giacomelli (Eds.),Fra Giovanni Angelico: pittore miniatore o miniatore pittore? Catalog of the exhibition in Florence, San Marco Museum, 20 December 2007–29 March 2008, Giunti, Firenze 2007, pp. 101–111.
[21] M. Picollo, A. Aldrovandi, A. Migliori, S. Giacomelli, M. Scudieri, Non-invasive XRF and UV-VIS-NIR reflectance spectroscopic analysis of materials used by Beato Angelico in the manuscript Graduale N° 558, Revista de Historia da Arte, Série W, 1, 2011, pp. 219–227.
[22] M. Scudieri, Frate Giovanni Angelico da Fiesole … eccellente pittore e miniatore, in: M. Scudieri, S. Giacomelli (Eds.),Fra Giovanni Angelico: pittore miniatore o miniatore pittore? Catalog of the exhibition in Florence, San Marco Museum, 20 December 2007–29 March 2008, Giunti, Firenze 2007, pp. 16–24.
[23] IFAC-CNR, Fiber optics reflectance spectra (FORS) of pictorial materials in the 270–1700 nm range, http://fors.ifac.cnr.it/ 2017, Accessed date: 30 November 2017.
[24] R. Jenkins, X-ray Spectrometry, Chemical Analysis, 2nd ed. Wiley, New York, 1999.
[25] M. Mantler, M. Schreiner, X-ray fluorescence spectrometry in art and archaeology, X-Ray Spectrom. 29 (1) (2000) 3–17.
[26] P.J. Potts, Introduction, analytical instrumentation and application overview, in: P.J. Pott, M. West (Eds.), Portable X-ray Fluorescence Spectrometry: Capabilities for In Situ Analysis, Royal Society of Chemistry, Cambridge 2008, pp. 1–12.
[27] C. Cucci, A. Casini, L. Stefani, M. Picollo, J. Jussila, Bridging research with innovative products: a compact hyperspectral camera for investigating artworks: a feasibility study, Proc. SPIE 10331, Optics for Arts, Architecture, and Archaeology VI, 2017 (1033106 (11 July 2017); https://doi.org/10.1117/12.2270015).
[28] Harris Geospatial Solutions, http://www.harrisgeospatial.com/Home.aspx 2017, Accessed date: 30 November 2017.
[29] F.A. Kruse, A.B. Lefkoff, J.W. Boardman, K.B. Heidebrecht, A.T. Shapiro, P.J. Barloon, A.F.H. Goetz, The Spectral Image-Processing System (Sips)-interactive visualization and analysis of imaging spectrometer data, Remote Sens. Environ. 44 (1993) 145–163.
[30] Harris Geospatial Solutions, Spectral Angle Mapper, http://www.harrisgeospatial.com/docs/SpectralAngleMapper.html 2017, Accessed date: 30 November 2017.
[31] C. Cennini, Il libro dell'arte, a cura di F, Brunello, Neri Pozza, Vicenza, 1971.
[32] R.H. Wilson, K.P. Nadeau, F.B. Jaworski, B.J. Tromberg, A.J. Durkin, Review of short-wave infrared spectroscopy and imaging methods for biological tissue characterization, J. Biomed. Opt. 20 (3) (2015) 030901.

[33] J. Plesters, Ultramarine blue, natural and artificial, in: A. Roy (Ed.), Artists' Pigments. A Handbook of Their History and Characteristics, Volume 2, National Gallery of Art, Washington 1993, pp. 37–66.
[34] J.H.R. Clark, Pigment identification by spectroscopic means: an arts/science interface, C.R. Chim. 5 (1) (2002) 7–20.
[35] M. Bacci, UV-Vis-NIR FORS spectroscopies, in: E. Ciliberto, G. Spoto (Eds.), Modern Analytical Methods in Art and Archaeology, Chemical Analysis Series, 155, Wiley & Sons, New York 2000, pp. 321–361.
[36] J. Rutherford Gettens, E. West Fitzhugh, Azurite and blue verditer, in: A. Roy (Ed.), Artists' Pigments. A Handbook of Their History and Characteristics, Vol. 2, National Gallery of Art, Washington 1993, pp. 23–65.
[37] B. Gilbert, S. Denoël, G. Weber, D. Allart, Analysis of green copper pigments in illuminated manuscripts by micro-Raman spectroscopy, Analyst 128 (2003) 1213–1217.
[38] P. Ricciardi, A. Pallipurath, K. Rosea, 'It's not easy being green': a spectroscopic study of green pigments used in illuminated manuscripts, Anal. Methods 5 (2013) 3819–3824.