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What non-invasive analytical techniques can reveal about 15th century illuminated manuscripts: an interdisciplinary study on the *Corali 43* by Beato Angelico

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Introduction

Among the several types of polychrome artefacts (panel paintings, frescoes, ceramics, pastels, etc.) illuminated manuscripts represent a very particular category, which requires special precautions and dedicated methodological protocols in scientific investigations. In the most general meant of the definition, an illuminated manuscript is a handwritten book adorned (*illuminated*) with colorful and finely painted decorations, letters, borders and miniatures, added to the text to enrich and underline the contents and the value of the book. Illuminated manuscripts constitute a quite articulated category of artefacts, including various typologies of ancient books, classified according to the epoch and place of production, the type of contents, production techniques and so on. [1]. From the point of view of conservation science, the main peculiarity of these artefacts is their inherent complexity, due to the heterogeneity and variety of constituting materials, and, often, to the multiplicity of artist’s techniques coexisting in a same book. Illuminated manuscripts feature colorful decorations and finely painted miniatures skillfully placed in the handwritten page to provoke a kind of lighting, luxurious effect. This impressive result was obtained using precious and varied pigments, and sophisticated artists’ techniques, often based on secret recipes and procedures, characteristic of each guild and workshop. All these elements, strictly linked to the geographical and historical context of production, are often unknown or scarcely documented and deserve an in-depth analysis. Another peculiar element of investigation on ancient manuscripts is that, in a same book, the simultaneous occurrence of excellent miniatures with less refined illustrations is likely found, thus getting more difficult the solution of attribution questions. Indeed, in the Early Renaissance, with the flourishing of illumination art in the Western Europe, the master illuminators were often important painters and famous artists, helped by their followers and assistants in making less important pages, details or depictions. However, available documentation about the authorships of an illuminated book is often scarce or unavailable. Within this framework, resorting to scientific analysis in order to identify constituent materials, pigments and dyes, and gain knowledge on manufacturing and artists’ techniques is crucial.

However, when dealing with ancient manuscripts, the plethora of analytical techniques usually available for artworks investigations is highly reduced. Indeed, in the majority of cases, microsampling techniques are not allowed, except when small detached fragments are available or if sophisticated ultramicrosampling methods are adopted [2]. Thus, the preferred option are non-invasive analytical techniques, although also in this case some practical limitation exists. For example, the fragility of supports (usually parchment or paper) limits the possibility of easily handling the book, or flattening the pages to access to any desired areas, and therefore optimized and cumbersome set-ups are often required to perform measurements. Moreover, the high light-sensitivity of manuscripts materials always dictates to minimize of the overall light exposure during a measurement session. Therefore, techniques using high intensity lighting should be operated under controlled and optimized conditions.

All these reasons encourage to seek for non-invasive and rapid techniques, suitable for investigations on illuminated manuscripts. Research in this area has progressively increased in recent years: portable Micro-Raman spectroscopy often combined with X-Ray Fluorescence demonstrated to be effective in a robust identification of pigments palettes in manuscripts [3-9]. Moreover, Visible (Vis) and Near Infrared (NIR) Reflectance Spectroscopy, implemented in both its 1D or 2D versions, that is as Fiber Optics Reflectance Spectroscopy (FORS) for spot-analysis and as hyperspectral imaging spectroscopy, has been successfully employed for identification and mapping of pigments and their mixtures, in illuminated manuscripts [10-14]. What clearly emerges from all published works is that none of the available techniques can be expected to be exhaustive, and for a complete identification of pictorial materials needed is always crucial to combine different complementary techniques.

Apart from being non-invasive, another key requirement for analytical techniques suitable for illuminated manuscripts is the possibility of collecting extensive and statistically meaningful data-sets. Indeed, a single book can contain a relevant number of scenes and several details of interest, spread out over numerous pages. Thus, portable, preferably hand-held, devices designed for fast and extensive analysis are highly desired, especially when comparative analysis between several pages are needed.

Given these premises, the development of robust experimental protocols, based on combination multiple techniques featuring non-invasive and rapid operability to acquire copious data-sets, could represent a further improvement for the systematic study of ancient manuscripts and their historical contextualization, which needs to cross many elements from stylistic, textual, historical and iconographic analysis.

This paper illustrates the results of a multidisciplinary study carried out on a precious illuminated manuscript, the *Corali 43*, dated approximately on first half of 15th Century and with a still uncertain attribution. The early studies on *Corali* 43 date back to the beginning of the 20th century [15]. The manuscript was at first ascribed to Zanobi Strozzi (1412- 1468), follower of Beato Angelico (1400-1455) - also known as Fra Giovanni da Fiesole or Fra Angelico - the book has been quite recently re-examined and new hypothesis about a possible attribution to the master Beato Angelico himself [16-19], or to another unknown illuminator of his circle, has been formulated. Despite its historical interest and its high artistic value, this manuscript was never investigated by means of analytical techniques before.

In this work the results of scientific analysis, performed for the first time on *Corali* 43, are presented. Different non-invasive techniques, such as Vis-NIR Reflectance Spectroscopy (FORS and hyperspectral imaging), XRF were used to identify the pictorial materials and provide information on the artists' techniques used to accomplish the miniatures and decorations within the book. Besides providing new elements to the art historians debate, this study contributes to a wider, long-dated research dedicated to the artistic production of Beato

Angelico and his followers. In 2007-2008, the San Marco Museum in Florence acknowledged with a special exhibition the eclectic figure of Fra Angelico, who excelled not only as illuminator, but also as wall and panel painter. This special event offered the occasion to study the relations between paintings and illuminations Angelico's production as well as to initiate a systematic survey of some the most representative manuscripts produced in 15th century in the Florentine area by the Angelico's entourage. The first outcome of this ambitious project was the scientific analysis on the *Graduale* 558, one of the most significant illuminated books certainly attributed to Angelico. The early studies on *Graduale* 558, published at first in 2007 the Florentine exhibition catalogue, were furtherly expanded is subsequent years [20,21]. The present work, now dedicated to the book *Corali* 43, is a further step in the survey of the Angelico's corpus manuscripts. The new data have been also compared with those acquired on *Graduale* 558, and new elements were gained to fill some of the lacks in the complex historical reconstruction of this historical context.

2. Materials and methods

2.1 The illuminated manuscript Corali 43

The *Corali* 43 (size 510 mm x 372 mm) is an Antiphonal produced as illuminated manuscript on parchment and dated between the third and the fifth decades of the 15th Century. A lack in documentation prevents a more precise chronologic contextualization of *Corali* 43 within the first half of 15th century. It contains 261 folia, nine of which illuminated with historiated initials and some of them with large and rich decorations and histories in the borders.

The ascertained facts about *Corali* 43 are few: it comes from San Domenico in Fiesole, a convent near Florence, venue of the community of the religious Dominican Order where Fra' Angelico became friar, lived and worked. The manuscript is supposed to have been kept 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 and available to the public.

The certain attribution of the manuscript, as well as its dating, remains unsolved. As said above, the miniatures of the book, at first attributed to Zanobi Strozzi (1412-1468), were recently supposed to be compatible with Angelico's style, although this hypothesis is still not completely accepted. Indeed, a complex panorama emerges from the art-historians debate. The originality of many iconographic inventions reveals the idea of a great artist, and it is logic to think to Fra Angelico, whose wall paintings are recalled in some scenes. Moreover, it is not easy to approach these illuminations to Zanobi Strozzi, who shows different characteristics in his later illuminated manuscripts. However, the style is not so close to Angelico's panels or to his known illuminations: the way of painting is fast, not refined. Furthermore, to the naked eye the *Corali* 43 appears particularly different from the Angelico's *Graduale* 558, coming from the same convent. Differences among the two manuscripts regard several aspects, such as the palette, in the choice of color combinations, and in the pictorial technique.

The iconographic and stylistic analysis of the several miniatures occurring in *Corali* 43 also highlighted some discrepancies among the different illustrated pages, and in some case within the same illuminated initial, thus suggesting a compresence of different hands [17]. Namely, whereas some miniatures show great quality and appear to be consistent with Angelico's production, other pages appear with fast and less refined traits, perhaps illuminated in collaboration with a less skillful artist.

The nine illustrated pages of the manuscript, classified as: ff.1r, 147r, 168v, 186r, 199r, 220r, 241r, 253r, 256v, are shown in Fig. 1. Beside the illuminated folios, other pages with decorated parts were also analyzed.

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 is 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 measurement campaign on *Corali* 43 was performed on 244 spot areas, selected according to the indications of art historians and curators, all over the painted illustrations and on selected decorations, including pen traits and inks.

The following pages were analyzed: f.8r, f.38r, f.46r, f.71r, f.95r, f.1r, f.147r, f.168v, f.186r, f.199r, f.220r, f.241r, f.253r.

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

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 × 7 mm in size. The spectra were collected at 40 kV and 12 µA with 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 page under analysis and from one or more underlying pages if written or painted areas are present. Taking this into account XRF measurements were performed by analyzing without drawing or paint on the back side. In addition, to exclude contributions from painting on other pages a PMMA (polymethylmethacrylate) slab (1 cm thick) was positioned below the page under investigation [24-26].

2.2.3 Hyperspectral imaging

A prototypal version of a new hyperspectral camera provided by SPECIM, Spectral Imaging Ltd. (Oulu, Finland) to IFAC-CNR as testing laboratory, [27] but not yet on commerce, was used to perform analysis on a sub-set of selected pages. The camera is very compact (207 x 91 x 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 on the 400-1000 nm spectral range with 7 nm spectral resolution. The measurements were performed by mounting the camera on a tripod, at a distance of about 50 cm from the target surface. The surface was illuminated using two Solux 50W 36° MR16, 4700° K light sources, selected to ensure a minimum lighting impact on this highly photosensitive object. The calibration was made using a certified white reference Spectralon® 99% diffuse reflectance target, framed together with the scene to be examined. The acquired data-cubes were elaborated using the software ENVI®. The IFAC-CNR Vis-NIR reflectance spectral library was used to extract end-members for implementing classification algorithms, such as the Spectral Angle Mapping (SAM).

3. Results and discussion

The primary aim of the non-invasive measurements campaign was the identification of the materials, pigments and their mixtures, used to accomplish the different miniatures.
At the preliminary visual inspection, the book appeared characterized by an uncommon variety of hues and colors, which was also indeed considered as a clue of different hands in making the illuminations.
The FORS data acquired on the selected areas were combined with XRF measurements to accomplish the data interpretation and provide a sufficiently exhaustive characterization of materials. However, to get more 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 pages constituting the manuscript are made of parchment. It is known that, according to the ancient recipes, the pages for illuminations were pretreated, 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 [28].
A FORS spectrum of an unpainted area has been acquired in each page, 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 parchment of different folios showed almost similar characteristics, and a typical example is reported in Figure 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 1200nm, 1500nm, 1750nm, 1900-2000nm are due to overtones and combination bands of the fundamental vibrational modes of hydroxide and water.
As reported in [29], the absorption features due to the methyl and methylene groups of the parchment are found in the same wavelength intervals than water and hydroxide. The absorption peaks at around 1730nm and 1690nm can be assigned to the first overtones of the symmetric and asymmetric stretching fundamental mode of CH_2 and CH_3 groups.
XRF spectra on two unpainted parchment spots revealed the presence of following elements: Ca, Fe as minor component and K in traces. 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.
The gold leaves, which were extensively used in the *Corali* 43 for background and aureole areas, were made with pure gold. The gypsum was present as a preparatory layer for the application of the gold leaves in mixture with iron(III) oxide 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, 1490, 1535 nm, due to the first overtones of the OH-streching of the reticular water, plus other water combination bands at approximately 1200, 1750 and 1945 nm.

3.2 The palette

Corali 43 shows an interesting and nice variety of hues, including blue, deep pink, red, green, yellow, and a set of color combinations, such as blue-pink, blue-yellow, green-deep pink, red-yellow, and red-green. The colors are usually very intense and vivid, except green shades which are usually pale, dull and most of the time with a particular yellowish tone. In addition, the brush strokes are pasty with white spots that increase the plastic effect of the figures and compositions.

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, which were indicated by art historians as deserving deeper investigations to shed light on the authentication and chronological issues linked to *Corali* 43.

3.2.1 Blue and bluish areas

Ultramarine blue and azurite were the two blue pigments detected in the manuscript. They are easily identifiable using FORS, since they have quite characteristic Vis-NIR reflectance spectra. According to the data acquired, ultramarine blue was the blue pigment most extensively used to paint the analyzed scenes. The color of natural ultramarine blue is due to a charge transfer electronic transitions inside the S^{3-} group that is present in the lattice of the complex alumino-silicate [30-31]. The Vis-NIR spectrum of ultramarine, as shown in Figure 3, has a characteristic strong absorption band centered around 600 nm, whereas in the NIR region it does not present any characteristic absorption band [32].

In Figure 3 two spectra acquired in blue areas visually slightly different (the points P12 and P13 in f.1r) are reported together with the reflectance spectrum of a reference material, a pure lapis powder. The comparison clearly shows that the both spectra perfectly correspond to a pure ultramarine pigment laid on the parchment support. Apart from the spectral features of the parchment, no other bands than those of lapis can be detected. This excludes, for these areas, use of mixtures of pigments (e.g. addition of white lead) to obtain the paler hue of background. 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 ultramarine blue without being mixed with lead white or other pigments

Azurite was used to paint the other blue areas. As an example, in Figure 4 the Vis-NIR spectrum of a measured point (P1) on the vest of Jesus is compared with the reference spectrum of azurite pigment, from the IFAC-CNR database, and with the spectrum of parchment.

Azurite is a basic copper(II) carbonate and its color is given by the electronic d-d transition of the copper(II) [32-33]. In the Vis range, azurite shows a reflectance peak at about 450-480nm and a broad absorption band in the 700-900nm range. However, for the present FORS device configuration, the actual diagnostic absorption band of azurite occurs at about 1500nm. This feature is evident in the pure pigment reference spectrum reported in Figure 4. It has to be noted that, although another diagnostic spectral features of azurite are in the 2200-2400nm region, the acquired spectrum on the mantle of Christ (P1) can be unambiguously identified as azurite. This result has also been confirmed by XRF, which found on the same area a significant presence of Cu with Fe, and traces of Ca, P, Si.

It has to be noted that the precious ultramarine blue pigment was not dedicated to mainly depict the most important and representative figures of the scenes, as expected, but, conversely, it was also used to fill background areas.

Ultramarine blue was extensively detected in most of the blue areas investigated. However, in some cases the FORS spectra acquired on blue areas in other pages presented different spectral characteristics. This was the case of f.168v, which is indeed considered by art historians stylistically different than most of others in *Corali* 43. The hues of this illumination appeared duller and with less vibrant hues, suggesting a possible different use of pigments and painting technique. The FORS spectra acquired on blue paints of f.186r presented different spectral characteristics, which suggested, in this case, the use of ultramarine blue probably in mixture with other pigments. The spectra of two spots, P1 and P4, corresponding to different hues of blue are reported in Figure 5. The comparison with the reference spectrum of powder of pure ultramarine blue shows a different behavior in the 500-1000nm region, likely due to the additional effect of other pigments, most probably a red lake.

Since the spectra acquired in P1 and P4 showed some differences between each other, likely different mixtures were used to paint these areas. In order to visualize the actual distribution of those mixtures/hues and to extend the spot size information to larger areas it was decided to use the hyperspectral imaging technique to reconstruct the distribution maps of these different mixtures and their abundances over the areas under analysis. The same scene was imaged using the camera and the corresponding data-cube was acquired [34].
SAM classification algorithm was applied to the data-cube acquired on the selected area. The two reflectance spectra (Figure 5a), extracted from the data-cube in correspondence of points P1 and P4, respectively, were used as end-members for SAM classification The result obtained is reported in Figure 6, where the P1 spectrum is mapped as blue and the P4 spectrum is mapped as green. This map indicates that the same mixture was used to make all blue details, except than the sky and the vest of the central figure, which resulted to be made with pure azurite from the FORS data (P22).

3.2. 2 Green areas: similarities and differences with coeval manuscripts

Generally speaking, the identification of the greens palette in illuminated manuscripts is 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 [35-36]. Green hues and shades were obtained not only with green pigments, but also with mixtures between blue and yellow pigments. This choice depended on several factors, such as the artist intention, the typical recipes and techniques of the illuminator workshops, the local availability of materials. Also in the case of *Corali* 43 the study of green areas in had a particular interest for the historical contextualization of the manuscript.
A set of 40 FORS spectra was acquired only on green areas, featuring different hues and intensities at the visual inspection. The majority of the spectra recorded showed similar spectral features which allowed to infer a predominant use of mixtures between yellow and blue pigments. As an example, the Vis-NIR spectra acquired on two the different greens (P11 and P12) selected in in f.147r are reported in Figure 7. Around 500nm, both the reflectance curves rise, indicating the presence of a yellow pigment. Two residual weak absorption bands centered around 630nm and 840nm, are instead attributable to the 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 1500nm. The different behavior observed in P11, in principle, could be explained with the presence of another blue pigment (ultramarine blue) or, alternatively, with a very low amount of azurite in the mixture. However, in case of mixtures, FORS can provide only a qualitative information. Moreover, 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 due to their spectral shape in the VIS-NIR region.

Therefore, XRF was used to corroborate the identification of these mixtures. In Figure 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 a lead-tin yellow was the pigment used in both the mixtures. In addition, the presence of Cu, detected in both the areas, but with a higher number of counts in P12, confirms the hypothesis of use azurite at different concentration rates in the two mixtures.
The analysis of the 40 greens spectra 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 at a lesser extent. This fact can be clearly observed in the overall view of all the FORS spectra acquired on green areas reported in Figure 9, where only few spectra with different spectral features are present. This sub-set of 40 spectra was processed with a statistical approach, in order to gain some insight 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 400-1000nm. The PC1-PC4 score plot reported in Figure 10 clearly shows a main group of data, associated to the spectra of green obtained as mixtures, and a separate cluster, which include the few spectra associated to pure greens pigments. The attribution of these data to the corresponding spot where they were acquired highlighted that these pure pigments were found exclusively on historiated letters, but not in illuminated scenes. Therefore, these data suggest that only mixed greens were used for depicting the illuminations.
This is an important element of difference with the *Graduale* 558, where, conversely, only green pigments, such as malachite and green earth, were found in the examined illuminations.

4. Summary of the analysis

The set of pigments identified consist of a limited range of basic pigments skillfully used to obtain a rich and colorful palette, accordingly with the habits of the Florentine circle of Beato Angelico. Specifically, the FORS spectra recorded on blue areas revealed the presence of both ultramarine blue (lapis lazuli) and azurite, being the former the most representative blue pigment. Ultramarine blue was also used in mixture with red pigments, red lake mainly, at different concentrations to depict deep pink-violet-purple details.
XRF data combined with FORS allowed to identify the yellows palette, which included essentially lead-tin yellow, used 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 presence of contemporary 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 trivalent iron are easily detected, and XRF spectra.
An accurate study conducted on green areas demonstrated that almost all green scenes were depicted using with yellow and blue mixtures, at different concentrations to obtain different shades and hues. A sporadic presence of a copper based green pigment, such as malachite, and green earth was detected in historiated letters and side decoration, but never in illuminations. This predominant use of mixed greens was considered a key information about this manuscript, since in the coeval *Graduale* 558 Beato Angelico used only malachite to create the green and greenish shades.
The red areas were obtained primarily with vermilion, detected by XRF due to the presence of mercury, and red lake, identified by FORS. Also red lead (minium) was found, even in association with vermilion. The red lakes were used mainly on the purple-violet glazes and to produce hues from pink to purple.

Lead white was extensively detected throughout the book, especially in mixtures with other pigments. Black areas were depicted with carbon based pigments, such as lamp black, bone black or vine black. All 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.

5. Conclusions

In the study of illuminated manuscripts, besides the identification of pigments and constituting materials, every additional element about the manufacturing process, the artist's technique and stylistic peculiarities may be precious gain 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 its two versions, as spot-analysis (FORS) and 2D hyperspectral imaging, together with portable XRF, demonstrated to be a powerful experimental chain to gain deeper insights on the case study examined, the illuminated manuscript *Corali* 43.
Thanks to their non-invasiveness and fastness in data acquisition, FORS and XRF were extensively applied on all the illuminations and on other significant decorated parts of the manuscript to obtain a copious data-set, statistically meaningful to provide the complete palette of the illuminated book. Subsequently, the additional use of a prototypal hyperspectral camera provided 2D Vis-NIR data of selected scenes, which were processed using classification algorithms (SAM) to map the distributions of pigments or mixtures over selected areas. These maps proved to be effective to easily visualize how extensively and where a given material or mixture was used, thus providing further elements on stylistic and procedural aspects not attainable with spot techniques. Specifically, hyperspectral imaging highlighted a singular use of blue mixtures in selected scenes, such as in f.147r, which considered stylistically different from the others within the book.
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.

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FIGURES and TABLES CAPTIONS

Figure1. *Corali 43*: the nine pages decorated with miniatures.

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

Figure 3. top) Vis-NIR reflectance spectra acquired by FORS in P12 and P13, corresponding to lighter and darker hues areas from the f.1r, compared with the spectra of a reference powder of pure lapis lazuli and of the unpainted support (P19). bottom) The f.1r and the detail with the measured spots.

Figure 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 and the unpainted support (P19). bottom) The detail of the illumination in f.1r and the location of measured areas.

Figure 5 Right) Vis-NIR reflectance spectra acquired by FORS on the sky (P1) and on the bluish area P4 of f.186r, and the reference spectrum of a ultramarine blue (Lapis ref.). Left) The detail of the illumination in f.186r and the location of measured spots.

Figure 6. Right) The detail of the illuminated letter in f.186v and (Left) the map of two different blues obtained using SAM. The pigment mixture used for the coffin is mapped as green-light, whereas the mixture used for the sky is marked as blue.

Figure 7. Left) Vis-NIR reflectance spectra acquired by FORS on the green of the capital letter "I" and on the foliage (P12) of f.147r. Right) The detail of the selected illumination in f.147r folium and the location of measured areas.

Figure 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 L□ line of Lead is out of scale for a better reading of the spectrum

Figure 9. The 40 FORS spectra acquired on all the green spots selected on *Corali* 43

Figure10. PC1-PC4 score plot from the PCA data analysis applied to the set of the 40 FORS spectra acquired on green zones.

Table 1 Pigments and dyes identified