

AN INTEGRATED AND ANALYTICAL APPROACH TO STUDY OF MURAL PAINTINGS: THE CASE OF “LO SPAGNA” IN SPOLETO

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Abstract

The present work shows the advantages of a multi-analytical methodology based on non-invasive and micro-invasive spectroscopic techniques in the study of wall paintings located in San Giacomo's church in Spoleto (Italy). The cycle of these mural paintings was realized by Giovanni di Pietro named Lo Spagna and his collaborators between 1526 and 1530. This study was focused on the characterization of pigments, in particular the blue ones, binders and degradation products to define the conservation state of these mural paintings and localize the repaints. Portable reflection infrared spectroscopy allowed us to identify the areas to be sampled to perform deeper analyses by scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS).

Keywords: - mural painting, blue pigments, reflection infrared spectroscopy, SEM-EDS

Introduction

Painting materials identification on archaeological works of art such as mural painting is an important task to better understand the materials and the painting technique, especially to select the most suitable conservation and restoration procedures. For this purpose, a large set of both non-invasive and micro-invasive analytical techniques are available. The use of traditional analytical methods to characterize artworks is difficult because it needs wide sampling procedures that are restricted or even prohibited. Non-invasive mobile instrumentation is a good tool to perform on-site analytical studies without causing any damage to artworks. Generally, this kind of approach provides enough information concerning the artwork but there are cases in which the collected data are not completed, and it is necessary to perform further analyses in the laboratory [1, 2]. Those cases need more information related to the stratigraphy of an artwork, that is pictorial, supporting and repaints layers [2]. Nevertheless, non-invasive in situ analyses are very useful because they allow the development of an efficient sampling strategy [3, 1]. This kind of approach is very suitable especially when a large area of the artwork must be analyzed, integrating non-invasive and micro-invasive techniques with the aim to identify the

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conservation state and the causes of degradation [4]. The spectroscopic techniques are the most used among all non-invasive analytical ones and, particularly, reflectance infrared spectroscopy allows the collection of data relating to organic and inorganic materials and degradation products [5-7]. The present work shows the usefulness of the complementary non-invasive and micro-invasive spectroscopic techniques to extensively examine painting materials and degradation products of mural paintings realized by Giovanni di Pietro named Lo Spagna. The cycle of mural paintings in the presbytery of St. Giacomo's church in Spoleto (Italy) were made by the artist Lo Spagna with his studio between 1526 and 1530. The apse cap depicts the Virgin's Coronation between Angels and Saints while in the presbytery there are two chapels designed by Spagna but painted by his workshop between 1527 and 1528 (Fig. 1). One of them, finished in 1527, is dedicated to Saint Sebastian and depicts the Madonna with the Child between cherubs and angels together with San Rocco, on the right, and the Ponziano Pope, on the left. The other one is dedicated to Saint Anthony abbot and illustrates the Madonna surrounded by angels and Saint Peter, Saint Anthony abbot and Saint Bartholomew. This one was probably realized after the death of Lo Spagna by Dono Doni and his collaborator Cecco di Bernardino [8]. Three important restorations have been executed during the 19th century [8] but in 2010 the vault collapsed and a restoration was necessary due to storm water infiltrations that have degraded the mural paintings. In particular, in the apse a lot of salt deposits were evident together with raising of the paint film and loss of pictorial material. Therefore, a diagnostic campaign was necessary to help the restorers particularly during the cleaning process of the blue areas of the sky and mantles in the presbytery paintings. To do this, non-invasive diagnostic analyses have been carried out by reflectance infrared spectroscopy to characterize the original materials, especially blue pigments, repainting and restoration materials and their distribution on the painting surfaces. After *in situ* analysis, five representative micro-samples were taken to analyze their stratigraphy by both optical and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) to overcome the limits of mobile instrumentation.

Materials and methods

Reflection mid-FTIR Spectroscopy

The portable infrared spectrophotometer ALPHA-R (Bruker Optik GmbH) is equipped with a Globar IR source, a patented interferometer (RockSolid™, insensitive to external vibrations and able to work in any spatial orientation) and a DLaTGS room temperature detector. The working optical layout for reflection measurements is 22°/22° (specular optics) with about 15mm of working distance. Its weight is approximately 7 kg and its dimensions are 20x30x12cm³. 200 interferograms in the spectral range 7500-375cm⁻¹ with a spectral resolution of 4cm⁻¹ were acquired. The sampling area was 28mm². A background correction using a reference spectrum from a gold flat mirror was applied for representing the reflectance profile (R) expressed in the graphs as pseudo absorbance, $\log(1/R)$.

Optical Microscopy

A preliminary evaluation of cross section and a study of the different layers was performed by a light-polarized microscope Olympus BX51TF, equipped with the Olympus TH4-200 lamp (visible light) and the Olympus U-RFL-T (UV light). The sessions were carried out in reflection mode at different magnification (10X, 20X and 50X).

Scanning Electron Microscopy (SEM-EDS)

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectra (EDS) were collected by using a Tescan FE-SEM, MIRA XMU series equipped with EDAX

spectrometer, at an accelerating voltage of 15–20kV, and high vacuum. The sample surfaces were metalized with a coating of graphite by Cressington 208HR sputter.

Results and Discussion

This section is divided in two paragraphs to illustrate the results obtained by non-invasive and micro-invasive analyses. In figure 1 the images of the analyzed mural paintings are shown.



Fig. 1. Mural paintings of the Saint Virgin's Coronation:
 a. images of apse cap depicts of Saint Virgin's Coronation;
 b. Saint Virgin with Child from Saint Sebastian chapel;
 c. Saint Virgin with Angels and Saints from Saint Anthony chapel

Non-invasive analyses

Non-invasive investigation campaign was carried out by means of reflectance FTIR spectroscopy on blue areas of apse, saint Sebastian and saint Anthony side chapel's mural paintings. The results are summarized in Table 1. In all analyzed points the presence of calcium carbonate is revealed by ν_2 and ν_3 bands at 874 and 1420 cm^{-1} respectively (Fig. 2) and the $\nu_1 + \nu_3$ combination bands at 2520 cm^{-1} [9], which are ascribable to the plaster of mural paintings. Gypsum and oxalates, identified by the ν_4 and ν_3 at 1120 and 670-600 cm^{-1} [10] and the symmetric stretching mode of CO at 1320 cm^{-1} [11, 12] respectively (Fig. 2), seem to be

uniformly distributed on the paint surfaces and are most likely the degradation products. The typical signals of azurite are observed in the blue areas of apse, along with the $\nu_1 + \nu_3$ combination bands at 2500, 2553 and 2590 cm^{-1} and the strong doublet at 4380-4244 cm^{-1} , ascribable to both combination $\nu + \delta$ and overtone three ν_3 (Fig. 3a) bands [5]. Azurite, most probably, is the original pigment, even though it is sometime mixed with lead white (Fig. 3a), identifiable by the $\nu_1 + \nu_3$ combination bands at 2420 cm^{-1} and ν_3 and ν_4 at 840 and 680 cm^{-1} respectively [13].

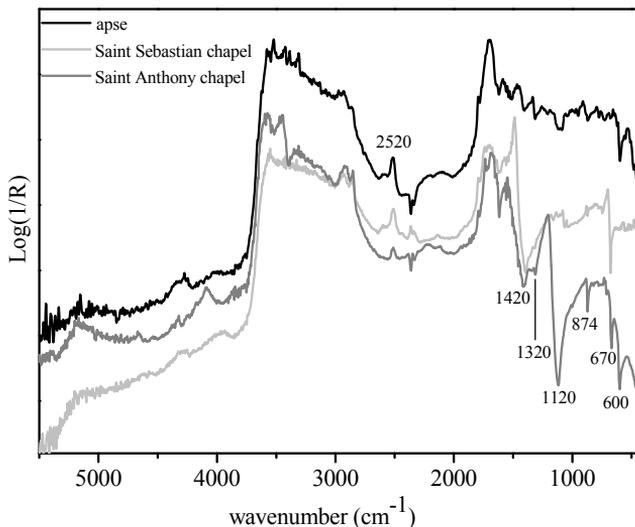


Fig. 2. Reflectance infrared spectra collected on different areas of apse (black line), S. Sebastian (light grey line) and S. Anthony chapels mural paintings (grey line).

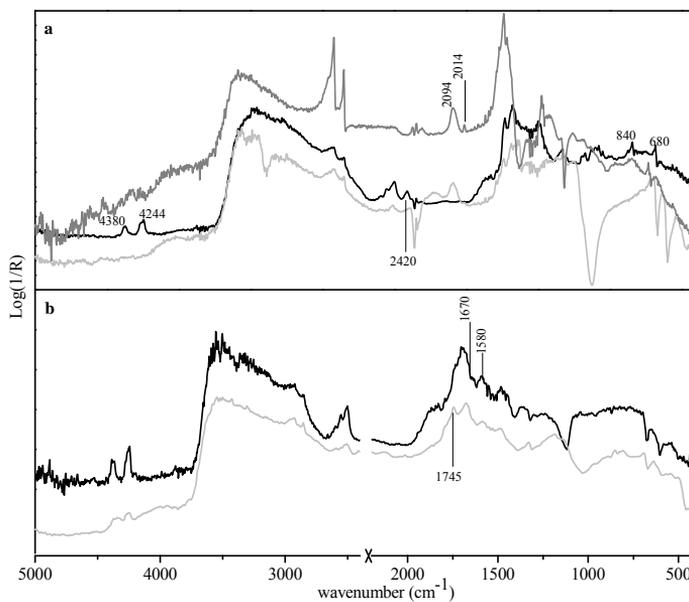


Fig. 3. Reflectance infrared spectra collected on the blue areas of apse (a) and representative of organic compounds found in the mural paintings (b).

In the blue areas of apse also the Prussian blue, employed as retouching pigment, has been detected by the CN stretching at 2094cm^{-1} [14], often mixed with ivory black to produce intense black shades (Fig. 3a), recognizable by the 2014cm^{-1} bands [6, 15]. The use of Prussian blue can be attributable to the first restoration by Giuseppe Carattoli in 1836 [8] who used the same pigment in the same years to restore the Benozzo Gozzoli frescos in San Francesco church in Montefalco [16]. The reflectance FTIR spectra collected on the blue areas of Saint Sebastian chapel showed the presence of lead white and Prussian blue while in the Saint Anthony chapel, beside weak signals of lead white, no infrared peaks typical of blue pigments were found. Therefore, it was possible to suppose the use of a synthetic ultramarine. By means of reflectance FTIR spectroscopy it has been possible to reveal the presence of organic compounds. Derivative bands at 1670 and 1580cm^{-1} and CH stretching with very weak intensity (Fig. 3b) may indicate the use of a protein binder [7] both in the apse and in the Saint Sebastian chapels, while CO stretching at 1745cm^{-1} and intense CH stretching at 2855 and 2920cm^{-1} are indicative of a lipid binder [7]. This one has been evidenced in the retouching areas in the apse, well visible to the naked eye and ascribable to the first restoration by Giuseppe Carattoli in 1836 [8].

Table 1. The studied mural paintings and outline of the main results obtained through the reflectance FTIR spectroscopy.

	Point of analyses	Results
Apsse	Blue campiture of angels	CaCO_3 , oxalates, lipid, gypsum, protein
	Sky	CaCO_3 , oxalates, azurite, lead white, gypsum
	Uncleaned areas	Prussia blue, gypsum, oxalates, CaCO_3
Saint Sebastian chapel	Retouching	CaCO_3 , oxalates, azurite, Prussian blue, lead white, lipid, gypsum
	Blue areas	Lead white, CaCO_3 , gypsum, oxalates, Prussian blue, protein
Saint Antony chapel	Blue mantle	CaCO_3 , oxalates, gypsum, lead white

Micro-invasive analyses

On the basis of non-invasive investigations, only some micro-samples were collected from different studied areas of the mural paintings trying to minimize any damage to the artworks. These micro-samples were taken using scalpels collecting the entire stratigraphy including the ground layer of mural painting. The analyses of these micro-samples were carried out on the polished cross-sections prepared with an epoxy resin. The sampling points and their brief description are illustrated in Table 2. In Figure 4 (on top) a cross section optical microscopy image of sample A_01, collected in visible light, is illustrated. Three different layers can be distinguished: an external blue one, an intermediate one of orange color and an internal layer of white color, ascribable to the plaster. The SEM-BSE image of this cross-section is illustrated in figure 4 (on bottom), where the red squares show the areas analyzed by EDS, while the results are reported in Table 3. In the blue layer, only the presence of copper (area 1) has been evidenced, suggesting the use of a blue copper based pigment such as azurite. The elemental analysis of orange layer (area 2) allowed hypothesizing the use of ochre while the white crystals (square 3) showed a significant amount of lead, ascribable to the use of a lead white. In figure 5a and 5b the optical microscopy image of AII-S2 cross-section are illustrated and three different layers, very similar to the sample A_01, are evidenced. Over the blue layer it is possible to observe another very thin layer not uniformly distributed, with a whitish color, probably made by an organic layer and aimed to protect the surface of the fresco. In figure 5c, the SEM investigation confirmed the presence of a homogeneous layer, made of crystals of various sizes, ranging from 5 to $40\mu\text{m}$. EDX analyses performed on the grains showed characteristic peaks of Cu, as illustrated also in the EDS map reported in figure 6. This result and the investigation of the cross section by optical microscopy [17] suggest the presence of azurite as also evidenced by the non-invasive reflectance Mid-FTIR analyses.

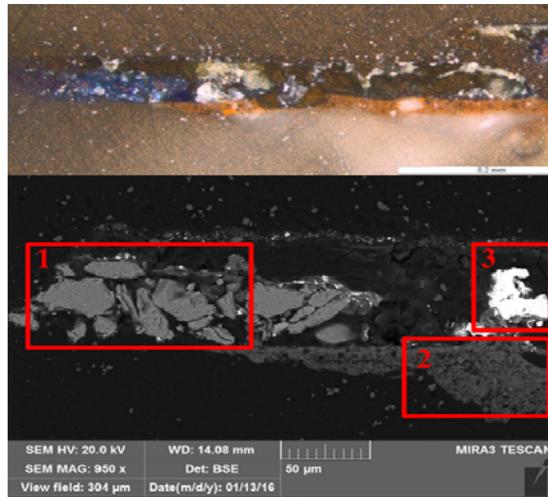


Fig. 4. Optical microscopy in visible light (on the top) and BSE images on the bottom (magnification 950X) of cross-section of sample A_01.

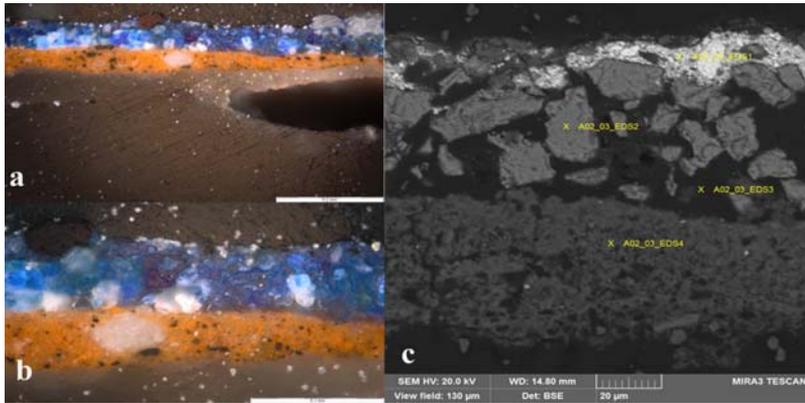


Fig. 5. Image in cross-section of sample AII_S2: a and b. Optical microscopy of in visible light; c. BSE images (magnification 2250X)

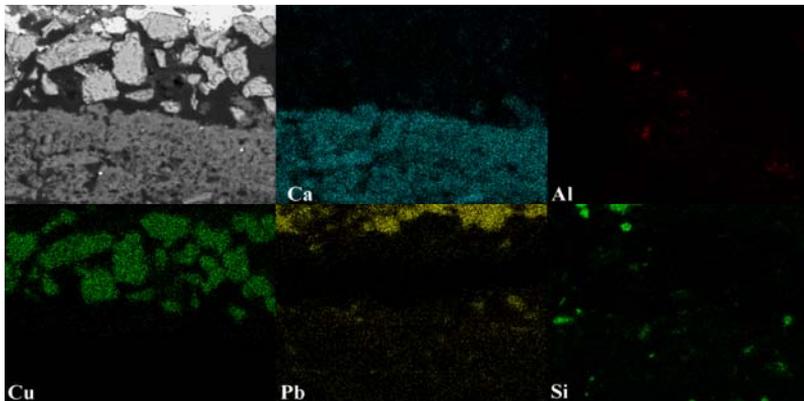
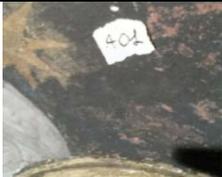


Fig. 6. EDS-SEM map of sample AII_S2

Table 2. Description of samples taken from the mural painting and images of their sampling point.

Sample	Description	Image
A_01	The blue sky in the apse	
AII_S2	Blue area in the sky of apse	
A_03	Gilded decoration in the blue sky of the apse	
CSS_S1	Virgin's blue mantle in the Saint Sebastian chapel	
CSA_P1	Blue sky close to the Angel in the right part of mural painting	

In the orange layer there are calcium, as predominant element, and silica, while lead and aluminum are present in minor amounts. The distribution of these elements is also well visible in the EDS map illustrated in Figure 6. These results indicate the use of ochre in mixture with lead white and calcium carbonate. The lead is also located in the upper layer in correspondence of the white grains visible in the BSE image (Fig. 5c) and in the EDS map of Figure 6. The red-orange layer on the apse is most probably the *fresco* preparation realized by ochre, which is the basis for the subsequent application of the azurite by a *secco* technique. This pictorial technique was found in other paintings by Lo Spagna and its disciples [18, 19]. The last sample taken in the apse (A_03) has been scrapped off from a star gilding decoration on the sky, partially covered by a blue layer.

The optical microscopy image in visible light (Fig. 7a) showed the presence of a very thick yellowish layer on top of which there is another thin yellow shiny one and a most external layer blue coloring. The SEM-EDS analysis (Table 3) collected on the yellowish ground showed the presence of lead, iron, silica as main elements and magnesium and sodium as minor components. These findings show the use of ochre in mixture with lead white. In the very thin yellow layer only the presence of gold has been recorded, as illustrated in the EDS spectrum reported in Figure 8, ascribable to the use of a gold leaf to realize the decoration. In the blue layer there is a significant amount of lead, suggesting the use of lead white in mixture with a

blue pigment, probably like Prussian blue, already used to cover the stars in the sky during one of the past restorations.

Table 3. Elementally analyses in weight % performed by SEM-EDS on the different samples. The areas/points analysed are shown in the BSE images of figure 4, 5, 7, 9 and 10.

	Area/point	Cu	Pb	Ca	Al	Fe	Si	Mg	Na	Co
A_01	1	64.7	---	---	---	---	---	---	---	---
	2	2.8	17.7	7.4	1.0	0.6	0.7	---	---	---
	3	6.8	63.4	0.5	0.2	0.3	0.35	---	---	---
AII_S2	1	---	71.6	2.2	---	---	---	---	---	---
	2	61.2	---	2.8	---	---	4.8	---	---	---
	3	---	5.6	53.9	0.5	---	---	0.2	---	---
A_03	1	0.9	74.7	0.4	0.3	0.5	---	---	---	---
	3	---	34.3	---	0.5	5.4	12.4	0.2	1.0	---
CSS_S1	1	---	69.6	0.3	0.3	---	0.6	---	0.2	---
	2	62.9	---	---	---	---	---	---	---	---
	3	---	---	48.7	5.4	7.5	3.8	0.5	0.2	---
CSA_P1	1	---	45.1	23.9	0.3	---	5.8	0.2	0.2	---
	2	---	12.7	21.0	4.7	5.2	6.0	2.8	---	24.9
	3	---	---	43.8	12.0	0.4	4.2	3.4	---	---

Sample CSS_1 has been scrapped off from the Virgin's blue mantle in the Saint Sebastian chapel. The optical microscopy image in visible light (Fig. 9a) showed the presence of four different layers: a white one, ascribable to the ground plaster, above which there is another orange layer. On top of the latter there are a coarse-grained blue layer and another homogeneous fine-grained layer with light blue color, where some white crystals can be clearly distinguished. SEM-EDS analyses, reported in the BSE image (Fig. 9b), evidenced in the light blue layer a significant amount of lead and traces of silica, sodium and aluminum, suggesting the presence of a white lead pigment, probably colored by synthetic ultramarine. In the blue layer, indeed, only copper has been found and on analyzing the morphological aspect of the blue grain, which showed a typical crystal habit of carbonates, the use of azurite as pigment can be ascertained.

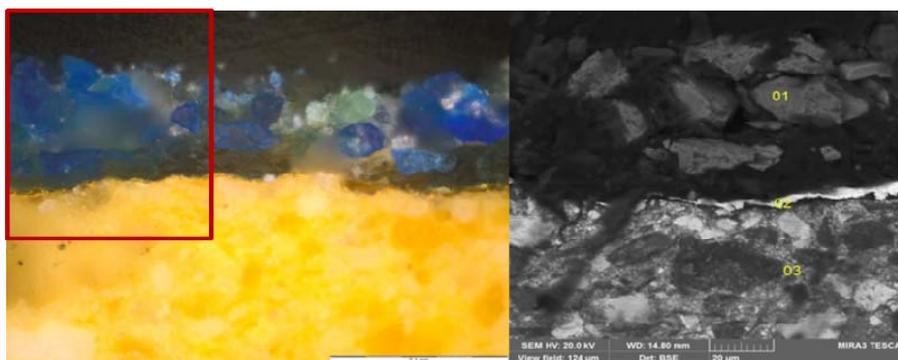


Fig. 7. Optical microscopy in visible light (on the left) and BSE (on the right, magnification 2370X) images of sample A_03

The orange layer seems to be constituted by typical chemical elements of ochre, like in the other cases discussed beforehand. In the Saint Anthony chapel, the sample CSA_P1 has been taken from the sky of the mural painting. Observing this cross-section by optical microscopy in visible light (Fig. 10a) it is possible to notice a fine-grained white matrix single layer with blue color crystals, having variable size and vitreous aspect. In Figure 10b the BSE image and the measurement points are reported. The EDS analysis (see Table 3) carried out in

the external layer of the cross-section showed the presence of lead, calcium and silica, while aluminum, magnesium and sodium are present as traces. These results led to suppose the use of a synthetic ultramarine as superficial restoration layer. The EDS analysis collected in the blue crystals evidenced the presence of Co, K, Bi and Al, typical elements of smalt [20]. The chemical elements found in the white matrix are characteristic for the plaster. From these results it is possible to infer that the smalt has been applied at *buon fresco*.



Fig. 8. EDS spectrum of golden leaf present in the cross section of sample A_03

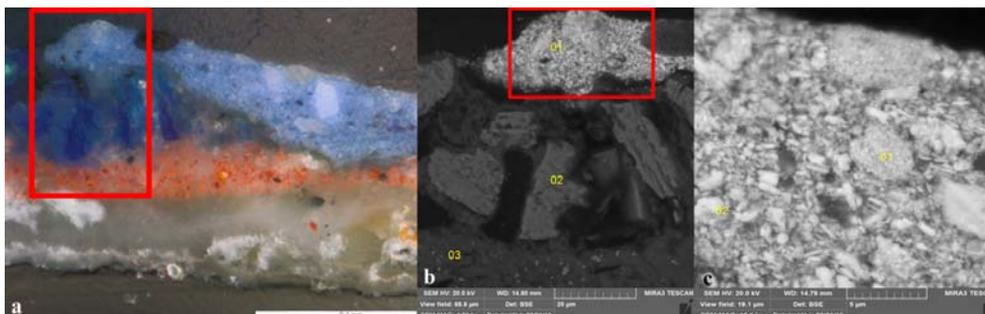


Fig. 9. Images in cross-section of sample CCS_1:
 a. Optical microscopy of in visible light;
 b and c. BSE images (magnification 4200X and 15000X respectively)

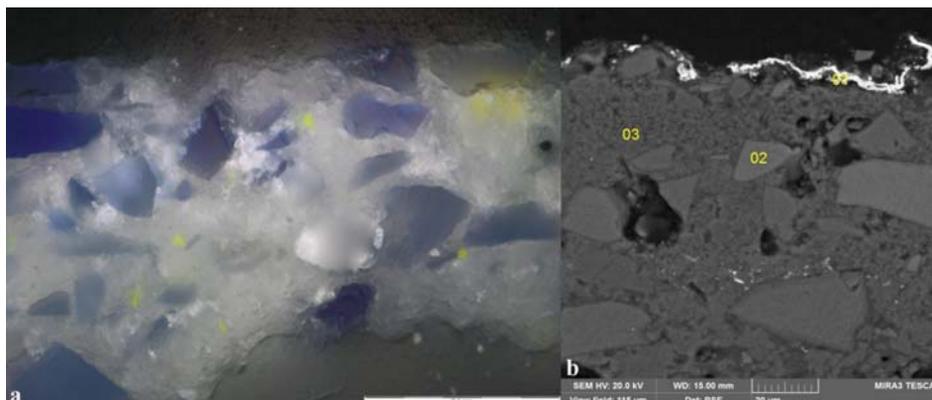


Fig. 10. Images in cross-section of sample CSA_P1:
 a. Optical microscopy in visible light;
 b. BSE image (magnification 4200X)

Conclusions

This work has shown how the use of an integrated multi-analytical approach is very helpful to study works of art. Specifically in this case, where extensive wall paintings had to be characterized, this methodology proved to be extremely effective since non-invasive investigations allowed to identify the different kind of blue pigments and their distribution map. This non-invasive work led to identify the most suitable points where to take five representative micro-samples for the cross-sections. Reflectance FTIR spectroscopy allowed to identify azurite, sometimes mixed with lead white, and Prussian blue, often mixed with ivory black, as both original and retouching pigments in the apse and San Sebastian chapel, along with degradation products such as oxalates and gypsum, uniformly distributed on the mural painting surfaces. Furthermore, some organic compounds have been identified as protein and lipid materials, most probably used as binders in the original and retouching areas, respectively. In all cross-sections optical microscopy allowed the identification of a red-orange layer over the plaster, made by a mixture of an ochre and lead white, as shown by SEM-EDS analyses. It is most probably related to Lo Spagna's typical ground preparation before the application of azurite. The observation by optical microscopy and SEM-EDS analyses in the Saint Anthony chapel showed that the blue sky has been realized using smalt as pigment, applied as *buon fresco* and covered by a thin restoration layer made up of a synthetic ultramarine pigment. In the cross-section taken on the Saint Sebastian chapel two different blue layers were evidenced by optical microscopy where azurite has been recognized in the original layer while for the more superficial one it was possible to hypothesize the use of a synthetic ultramarine. In the apse the presence of azurite as original blue pigment, and a golden leaf used by the artist to realize the starry sky have been revealed by SEM-EDS analyses. In conclusion, by means of this integrated multi-analytical approach, it has been possible to identify the different techniques ascribed to several Masters, who realized the cycle of mural paintings in the presbytery of St. Giacomo's church in Spoleto supporting the attributions of art historians. The apse and San Sebastian chapel were painted by a *secco* technique and the blue pigment used by Lo Spagna was azurite applied over an orange-red preparation layer, realized mixing an ochre with the lime. On the contrary, the Saint Anthony chapel, attributed to Dono Doni, was painted by a different technique: the smalt as blue pigment was applied as a *fresco* without the orange-red preparation.

Acknowledgments

The authors gratefully thank the Soprintendenza Archeologica, belle arti e paesaggio dell'Umbria and the Arcidiocesi di Spoleto-Norcia for allowing non-invasive and micro-invasive analyzes on the mural painting of Lo Spagna in the San Giacomo's Church in Spoleto. The diagnostic campaign was carried out within the framework of the Regione Umbria project "*Sviluppo e sperimentazioni di prassi, procedure e tecniche in ambito di diagnostica-prevenzione-conservazione*", APQ 2007 "Tutela e prevenzione dei beni culturali". Thanks to the restorer dr. Marcello Labate for all information provided and for supervising the diagnostic investigations.

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Received: October 14, 2017

Accepted: August 20, 2018