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DIAGNOSTIC INVESTIGATION THROUGH MINIMAL SAMPLING FOR RELIGIOUS ARTWORKS KNOWLEDGE

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Abstract

This contribution, starting from the fundamental assessment that artworks are unique and not-reproducible objects, reports the minimum investigation approach on some case studies, i.e. an approach based on a limited number of sampling points to obtain the maximum information as possible. This approach is particularly relevant and useful for investigating degradation patterns and material composition of artworks during a restoration process so that to correctly evaluate and choose the conservation strategies.
Sampling techniques have been performed in relation to the artwork typology and to the information requested by conservators before or during the intervention. This information generally concerns the knowledge of the execution technique, of the state of preservation, of the materials, and of the possible dating, but is gathered with few analysis and samples in order to limit the invasiveness.
The case studies selected for this paper are: the 16th century panel painting representing Saint George and the Dragon attributed to Raffaello; the 16th century canvas painting attributed to the Italian artist Cesare Nebbia depicting the pool of Bethesda, and one of the four 18th century medallions made of paper rags and representing life scenes of Saint Giacinta Marescotti from Viterbo. In all cases the minimum investigation approach demonstrated valid in supplying to the conservators the information requested, also with a single sample, and further data that could be gathered thanks to the availability of unexpected presence of micro-fragments in the sample/samples.

Keywords: cultural heritage, conservation, optical microscopy, SEM, FTIR

1. Introduction

Cultural heritage must be considered an expression of the intellectual richness and of the cultural differences of the modern societies, so its protection and valorisation should be imperative [EN16141, Conservation of cultural

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heritage - Guidelines for management of environmental conditions – Open storage facilities: definitions and characteristics of collection centres dedicated to the preservation and management of cultural heritage, CEN386, Bruxelles, 2010]. In fact, cultural heritage, besides having historical interest, supplies aesthetic, environmental and economic advantages to the countries. The conservation of cultural heritage implies its knowledge, not only from the historical but also from a material point of view. The knowledge of cultural heritage is often a challenge due to the variability of materials and construction techniques, to the scarce information about the conservative history of the artworks that certainly influenced the present state of conservation [1-3].

A diagnostic campaign should have the aim of collecting as much information as possible in order to define the execution technique and the state of preservation of the artworks to support the conservation and restoration process [4-9]. At the same time it is particularly relevant, and often neglected, to monitor the conservative environments (museums, churches, private collections, public expositive spaces, etc.) because they influence the material behaviour over time [10-12].

In the past and until recently, the diagnostics was not considered a fundamental step in a restoration or conservation process and the decision was based on the practical experience of the conservators: this approach has been demonstrated un-effective and sometimes even detrimental for cultural heritage objects [13]. However, at present the investigation of artworks through different and increasingly technological advanced methodologies, especially in case of restoration processes, is becoming widespread and it is considered as fundamental step for correctly performing the conservative projects [14]. So, especially in the case of restoration of important artworks, a lot of and sometimes useless analyses are performed, due to the visibility of the objects, whereas in all other cases few or no investigation is carried out usually for the lacking of time and economic resources specifically devoted to the diagnostics [6]. In those cases, according to our experience, the choice of making analysis is addressed by the conservator and depends only on his/her experience and sensitivity. For this reason it often occurs that, on the occasion of a restoration, few and specific analyses are requested by conservators, generally during the intervention as a consequence of particular problems of cleaning or consolidating. The minimum investigation approach is thought for these specific cases where one or two precious samples are available and they must supply as much information as possible [8]. According to this approach, frequently used in the restoration practice, three case studies are described and discussed in the present paper: 1) the 16th century panel painting representing Saint George and the Dragon attributed to Raffaello, 2) the 16th century canvas painting attributed to the Italian artist Cesare Nebbia depicting the pool of Bethesda, and 3) one of the four 18th century medallions made of paper rags and representing life scenes of Saint Giacinta Marescotti from Viterbo.

2. Case study 1 - the 16th panel painting representing Saint George and the Dragon

San Giorgio e il Drago (Saint George and the Dragon) is a panel painting (cm 21.1 x 27.5), dated to the first half of the 16th century and exposed in the Municipal Art Gallery of Spoleto, a small town in Central Italy (Umbria region) [15]. It is a high-quality and well-preserved artwork representing Saint George on horseback. From the iconographic point of view, he belongs to the typology of legendary saints. Saint George is represented in the act of fighting the dragon, which is the emblem of evil for Christianity. The painting has been considered a copy of the homonymous artwork by Raffaello Sanzio stored in the National Gallery of Washington, which is traditionally referred to a gift of the Duke Guidobaldo from Montefeltro for Henry VII of England, as a gratitude expression for having been awarded the Order of the Garter. After many events, the *San Giorgio* of Spoleto, was brought from France to Reggio Emilia around 1924 by the antiques dealer Luigi Parmeggiani whose widow donated it to the Art Gallery of Spoleto in 1954 [https://www.beni-culturali.eu/opere_d_arte/scheda/-san-giorgio-uccide-il-drago--10-00044234/455007].

The painting is characterized by the presence of a technique known as 'incamottatura', a canvas applied on wood to cover wood defects. In fact, the panel, built by the wood craftsman according to the indications of the painter, was sometimes made of several boards with defects, such as knots, which needed to be covered or repaired with sawdust mixed to glue. The continuity of the surface was re-established with the canvas and then with several layers of gypsum/glue characterized by different granulometry of gypsum [16]. Once the ground had been completely dried, the surface was scraped to obtain a smooth and homogeneous surface.

In this case, the restorer sent us a sample of 'incamottatura' with the request to characterize the fibre species and its morphological characteristics. Since the micro-fragment contained little pieces of wood and traces of pigments, it was decided to take advantage from this presence, for characterizing also the wood species and pigments, maximizing the results obtainable from a single sample [17].

3. Case study 2 - the painting by Cesare Nebbia representing the pool of Bethesda (dated back to 1594)

The oil painting representing the pool of Bethesda (319 x 201.5 cm) is considered a masterpiece of the Italian artist Cesare Nebbia (1534-1614) [http://www.asl.vt.it/News/immagini/2008/dipinto.jpg]. The painting was commissioned in 1594 for the Chapel of the Great Hospital of Invalids in Viterbo and at present it is stored in the conference hall of Brugiotti Palace, in the same city [18].

The painting was created on a so-called 'damask canvas' characterised by a lozenge structure, particularly diffused during the 16th and 17th centuries. This

kind of support gave the artist a robust surface that favoured the colour adhesion, thanks to the elaborated weave, which remained visible even after the painting application also allowing peculiar light effects [18, p. 113].

The painting underwent a restoration between 2006 and 2008 that was aimed at removing the 19th century lining, substituting it with a modern system able also to consolidate the original canvas and the painting layer, cleaning of surface altered materials and of dirt, adding a new suitable support structure as a replacement of the non-original one. The non-original frame, added on the occasion of the 19th century restoration, was made of chestnut and it resulted particularly heavy. For this reason, it was substituted with a new light aluminium based frame [18, p. 109].

During the restoration performed in 2006-2008, a sample was taken by the conservators in order to study the fibre species and its morphological characteristics. Also in this case study, since the micro-fragment contained little pieces of painting, it was decided to take advantage from this presence for characterizing also the binders and the pigments, maximizing the results obtainable from a single sample.

4. Case study 3 - one of the four 18th century medallions made of paper rags and representing life scenes of Saint Giacinta Marescotti from Viterbo

The researches performed on the occasion of the bicentenary of the canonization of Saint Giacinta and addressed to the so-called 'Giacinta days', allowed for discovering four painted and modelled medallions, made of paper rags, in the Monastery of Saint Bernardino in Viterbo. These objects were exposed in 1727 during the ceremony organised for celebrating the beatification of Giacinta Marescotti, a professed nun of the third Order of Saint Francis [19]. The discovery of such artworks was very interesting because they have been generally considered ephemeral artefacts, even since their designing: they were used for the ceremony and then discarded [19, p. 7].

The medallions were created through a specific procedure carefully described in the '*Vocabolario Toscano dell'Arte e del Disegno*' (Tuscan Dictionary of Art and Drawing) by Baldinucci in 1681 [20]. The pieces of rags and paper were soaked in running water for some days, then were pounded in a mortar in such a way to obtain a paste that had to be whitened. This was obtained by adding indigo blue pigment that gave the paste a cold hue compensating the yellow one: the whitening was so obtained for chromatic compensation [21].

The paste, after whitening, was spread in a gypsum matrix and pressed with a sponge for eliminating the water. After drying, the obtained mould was reinforced with canvas strips and glue and was completely dried in the sun or on the fire. The piece was reinforced and waterproofed with Greek pitch and covered with a layer made of gypsum and glue that constituted the ground for painting. At last, the external profile was outlined according to the desired form

of the so-called *laurata* crown [19, p. 35]. The obtained mould was then anchored to the wood support, as visible in the Figure 1.

Figure 1. The medallion representing 'The praying blessed Giacinta' after the restoration, front and back sides. The white circle identifies the sampling area.

The painting was applied by tempera, generally based on gum Arabic as binder that acted as protective of the pictorial layer too [19, p. 33-41].

The medallions appeared degraded with evident abrasions, folding and tears. The wood structures were clearly interested by local xylophages attack and were partially disconnected [19, p.43-44]. During the restoration work two samples were taken from the medallion representing 'The praying blessed Giacinta', in order to examine the fibres and the binder of the painting layer. Also in this third case, the two samples were examined in order to gather as much information as possible through the available laboratory techniques.

5. Experimental

In all cases, samples were preliminarily investigated by the Olympus SZ stereomicroscope in order to separate the different parts (fibres, wood, painting layers) for the other analyses. Fibre, pigments and cross section were examined under the Zeiss Axioskop polarizing microscope equipped with Zeiss AxioCam digital camera. Fibres and wood fragments were also studied through Scanning electron microscope (SEM) Jeol model JSM-5200 to better define the morphological and anatomical characteristics. The fragment and the fibres were sputter-coated with gold in a Balzers MED 010 unit in order to observe them under SEM. The wood taxa identification was performed according to literature dichotomous keys and descriptions [22, 23].

Organic binders were investigated through infrared spectroscopy by using a Nicolet Avatar 360 spectrometer. The instrument operated in the MIR spectral

range (400-4000 cm-1) with a resolution of 4 cm^{-1}. Micro-samples were mixed with spectrophotometric grade potassium bromide (KBr) and inserted in the DRIFT (Diffused Reflectance Infrared Fourier Transform) accessory. KBr was used also as background.

The smallest samples were analysed without any further treatment under the IR Centaurμs microscope both in micro and ATR (Attenuated Total Reflection) modality.

6. Results and discussion

6.1. Case study 1 - Saint George and the Dragon

The results of the analysis performed on the panel painting representing Saint George and the Dragon have been previously reported and here a synthesis is considered [17]. The observation with polarizing microscope of the textile fibres, embedded in Canada Balsam, showed morphological features that indicate the flax fibres (*Linum usitatissimum*). In particular, the fibres appeared cylindrical, uniform, with a thin central canal [17, 24]. They showed breaking nodes and intersection points or fine transversal striations often arranged in X-shape. These details, above all the uniform pattern of the fibres and the breaking nodes, were better detected under SEM [17]. The drying test performed on a small bundle of fibres under the stereomicroscope confirmed the identification of flax which, during drying, undergoes clockwise rotation [24, p. 79].

The micro-sample contained also fragments of wood, attached to the fibres, so it was decided to try the possibility of identifying the species, even if it was not requested by the conservators. The observation of wood micro-sample by optical and electron microscope, showed that the growth ring was incomplete [17, p. 117]. The wood originated from a broadleaf species, presenting solitary vessels or radial rows of two elements in cross section. It could be diffuse porous. The rays were exclusively monoseriate. This feature was confirmed observing the tangential section. The radial section highlighted vessels with simple perforation plate; wall vessels with alternate pitting and without spiral thickening. The rays were homogeneous with procumbent cells, showing large pitting between ray cells and vessels. All these features allowed for identifying poplar (*Populus* sp.) wood, one of the most widely used in Italy. The species of the genus *Populus* cannot be distinguished on the basis of the anatomical features of the xylem [6, 10].

The micro-fragments contained also traces of pigments that have been analysed through polarizing microscope under visible and ultraviolet radiation. Optical analysis of pigments suggested the presence of ultramarine blue, lead white and red lake (Figure 2). Ultramarine blue and lead white are characterized by very small particles; red lake is visible embedded in the greatest grain on the right side of the image in Figure 2A. The yellow fluorescence observed under UV radiation of microscope, suggests the use of siccative oil binder for pigments (Figure 2B).

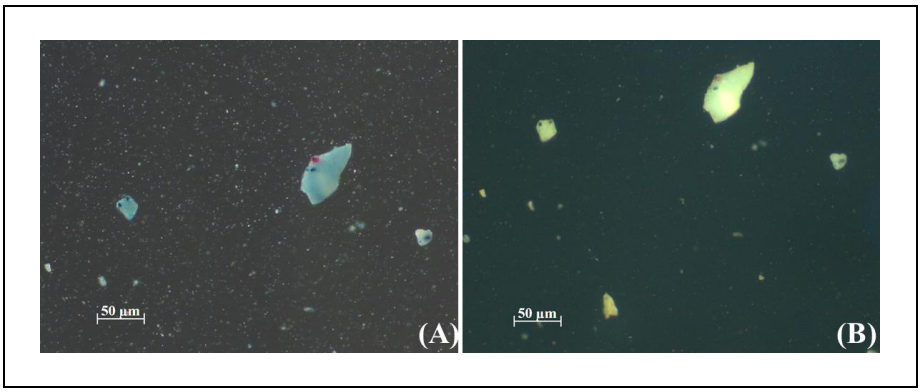

Figure 2. Microphotographs of painting micro-grains from the painting Saint George and the Dragon under polarizing microscope: (A) crossed polars, (B) UV fluorescence.

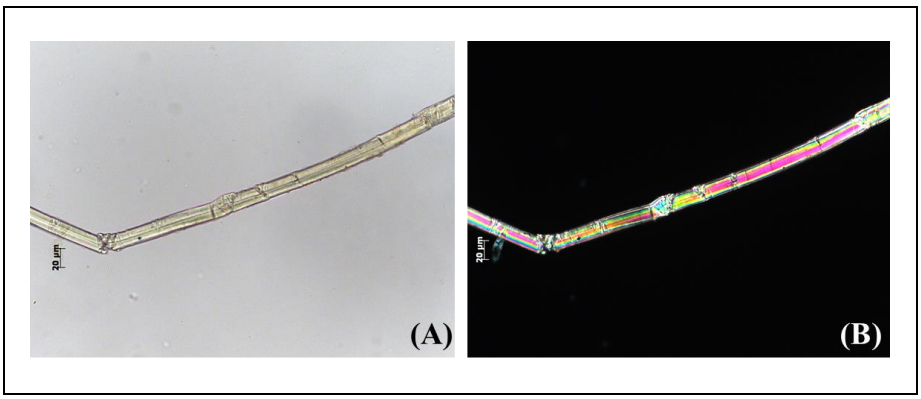

Figure 3. Microphotographs of a fibre from the painting of Cesare Nebbia under polarizing microscope: (A) parallel polars, (B) crossed polars.

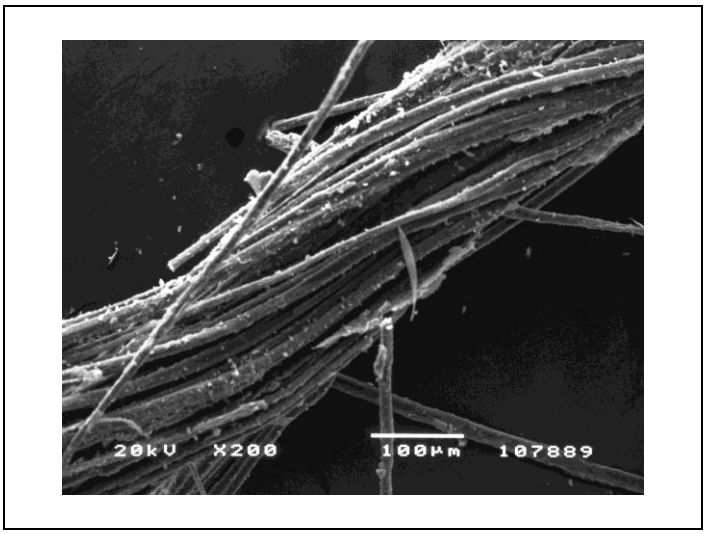

Figure 4. SEM microphotograph of a fibre bundle with the typical counter clockwise torsion of hemp.

6.2. Case study 2 - The pool of Bethesda by Cesare Nebbia (about 1594)

The first step of the analysis was addressed to the identification of fibres through examination under polarizing microscope, as requested by conservators (Figure 3). The morphological characteristics and the dimension of the fibres, compared to those found in literature databases, allows for hypothesize the use of hemp (*Cannabis sativa*) for the painting canvas [24, p. 18]. Hemp fibre are similar to those of flax so further investigation is required for a certain identification.

In particular, the textile fibres have been observed by SEM in order to detect further characteristics, not visible under polarising microscope. The image acquired through electron microscope of a fibre bundle highlights the counter clockwise torsion typical of hemp (Figure 4).

Taking advantage from the presence of a micro-fragment attached to the fibres, a cross-section was obtained (Figure 5). The cross-section allows for observing the transversal profile of the textile fibres, that appear rounded without marked polygonal aspect, this last one being typical of hemp. Flax and hemp are very similar and so difficult to be differentiated if observed only longitudinally. The cross-section under ultraviolet radiation also shows yellow fluorescence concentrated in the surface layer that can be attributed to oil siccative binder.

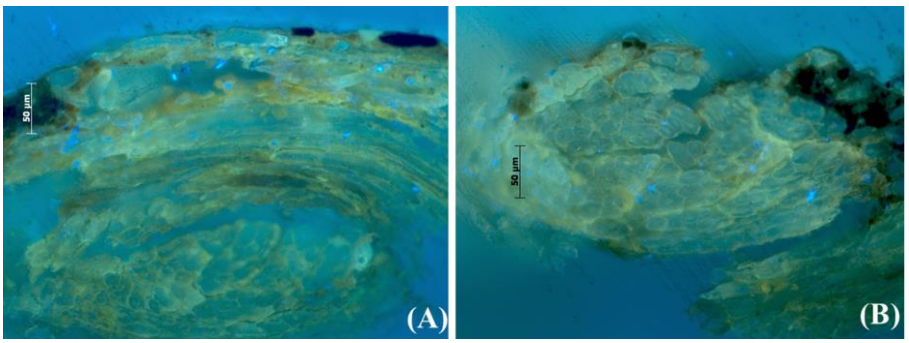

Figure 5. Microphotographs of the cross-section of a fragment from the painting of Cesare Nebbia, under polarising microscope, ultraviolet fluorescence: (A) fibres and traces of the painting layer, (B) detail of the fibres section.

The other information requested by conservators was related to the painting binder characterisation, which was obtained through Fourier transform infrared spectroscopy performed on a micro-fragment attached to the fibres [25, 26]. The IR spectrum is shown in Figure 6.

The spectrum is particularly rich of absorption bands suggesting the presence of different compounds. Band assignment for the main compounds is made in Table 1. The presence of gypsum and proteins indicates the use of a classical ground, made of a gypsum-glue mixture. Siccative oil is the binder of

pigments. A weak absorption at about 2340 cm^{-1} suggests the presence of ultramarine blue as pigment [25, p. 134-138]. At last, the absorptions at 1275 and 910 cm^{-1} show the presence of a natural resin that could be used for the final varnish of the painting.

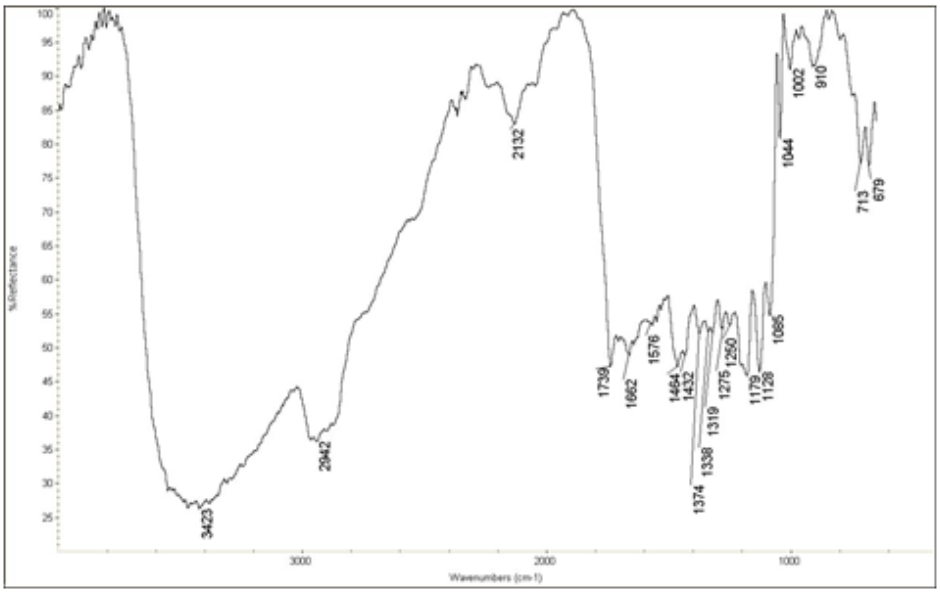

Figure 6. FTIR spectrum of a micro-fragment from the painting of Cesare Nebbia.

Table 1. Band assignment in the infrared spectrum of the micro-sample from the painting by Cesare Nebbia.

Absorptions (cm^{-1})	Band assignment
2942, 1662, 1555, 1464, 1374, 1338, 1319, 1250, 1085	Proteins
1739, 1464, 1432, 1179, 1002, 713	Siccative oil
2132, 1128, 1044, 679	Gypsum

6.3. Case study 3 - The medallion of Saint Giacinta Marescotti (1727)

The preliminary observation of the sample through stereo-microscope highlights that the paper used for creating the medallion is made of scarcely compressed fibres (Figure 7A). Blue, white and rare red fibres are detected and separated for observing them under polarising microscope (Figures 7B-D). The morphological characteristics of the fibres indicate the presence of both hemp and flax, this last one more regular and smaller fibres than those of hemp [24, p. 78, 81].

The careful observation of the sample under polarising microscope, allowed for detecting also the presence of blue grains attached to the fibre Figure 7E). These blue grains seem to be made of indigo, an organic dye used as optical bleaching during the 18th century and known as 'turchinetto (bluing)' in the

historical sources [21, p. 68]. Indigo was confirmed by micro-Raman analysis performed on the blue grain (data not shown).

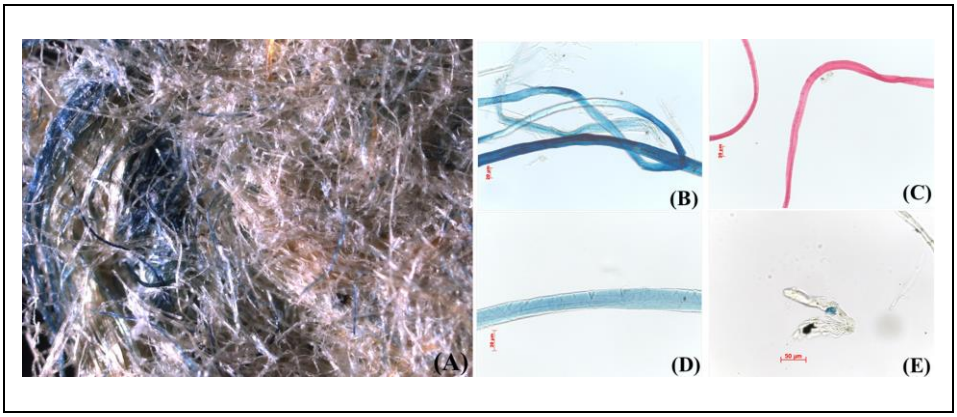

Figure 7. Microphotographs of the sample fibres: (A) a view under the stereomicroscope making visible the blue fibres, (B) some isolated blue fibres of different dimensions, (C) red fibres, (D) a single flax fibre, (E) a fibre fragment with a blue grain attached.

The investigation of fibres was completed by SEM (Figure 8). The microphotographs acquired through the scanning electron microscope confirmed the presence of hemp characterised by the typical counter-clockwise torsion (Figures 8A and 8B). In some areas the compression of the fibres may be observed together with the different dimensions of hemp and flax fibres (Figure 8C). The compressed fibres appear altered due to the beating used for obtaining the paper rags.

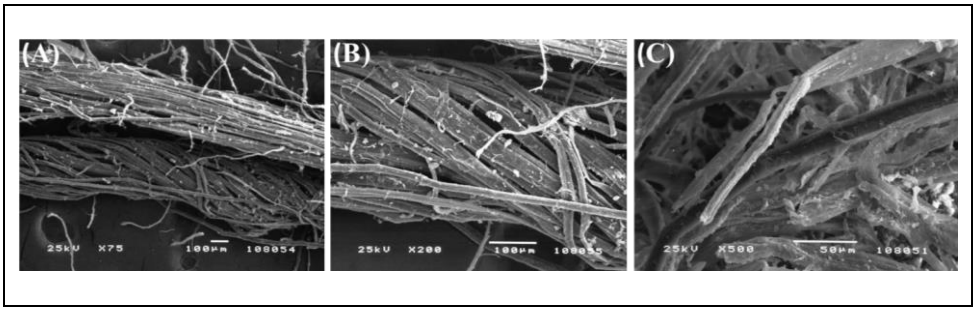

Figure 8. SEM microphotographs of the sample fibres: (A) a general view of bundle torsion, (B) a detail of (A) highlighting the torsion of hemp fibre bundle, (C) compressed and degraded fibres.

Organic binders were characterised by FTIR and micro-FTIR spectroscopy. The obtained spectrum is displayed in Figure 9. The main absorptions in the spectrum (cm^{-1}: 3427, 2922, 1733, 1627, 1426, 1325, 1269-1041) are typical of gum Arabic, a polysaccharides widely used in painting materials and also as surface protective [25, p.178; 27].

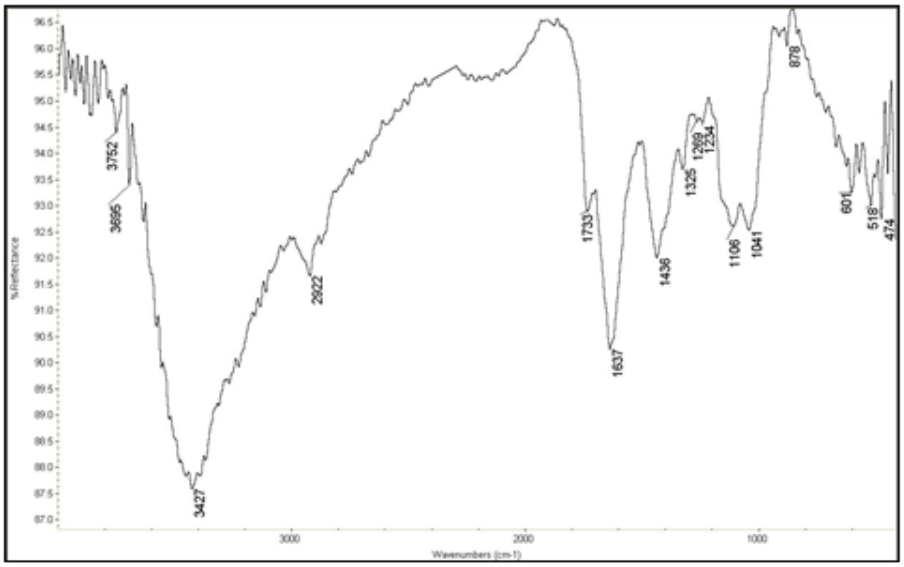

Figure 9. FTIR spectrum of a micro-fragment from the medallion of Saint Giacinta.

7. Conclusions

In this paper a new approach in the diagnostics applied to cultural heritage has been presented and discussed. This approach is based on the possibility of obtaining as much information as possible from minimum sampling performed during the restoration to solve specific problems. The idea of this approach derived from the experience with conservators that often sent to our diagnostic laboratory samples for analysis because they encountered problems during the restoration. The possibility to have one or two micro-samples gave us the opportunity to obtain not only the information requested by conservators, but also to gather further knowledge of the artworks.

The proposed approach has been reported for three case studies: the 16th century panel painting representing St. George and the Dragon, the canvas by Cesera Nebbia (about 1594) and depicting the pool of Bethesda, and the paper rags medallion representing 'The praying blessed Giacinta' (about 1727).

In the first case, the most relevant additional information was the characterization of the wood species (poplar) used for the support, thanks to the possibility of examining a very small fragment remained attached to the textile fibres.

In the case of the pool of Bethesda, apart from fibres characterisation, it was possible to investigate the binder of the painting taking advantage from the presence of a painting micro-fragment.

At last, the case study of the medallion of Saint Giacinta Marescotti allowed for obtaining information on the paper rags composition but also the interesting technique for bleaching the fibres through the use of indigo, a natural optical bleacher, confirming the historical sources.

In conclusion, the minimum sampling approach revealed useful for obtaining the maximum information on artworks. This information has been relevant for the restoration but it also constitutes a precious support for future studies and for desirable maintenance operations.

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