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A SURVEY ON THE POLYCHROMY AND PREVIOUS TREATMENTS OF THE XIV CENTURY MARBLE *ARCA AVOSCANO* IN THE BELLUNO CATHEDRAL (IT)

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ABSTRACT
A careful inspection of the Arca Avoscano funerary monument carried out during preliminary investigations allowed us to discover some traces of polychromy and gilding partially covered by grey airborne particulate deposits. In order to assess the polychromy and the gilding areas a preliminary analysis for the identification of elemental chemical composition of pigment traces by using a non-invasive application of a portable X-Ray Fluorescence (XRF) spectrometer was carried out. In some areas ambiguous results were obtained and therefore a subsequent stratigraphic examination was necessary to avoid any misinterpreting about the pigment layer stratigraphy. For this reason a successive non-invasive sampling was carried out and Environmental Scanning Electron Microscopy (ESEM) observations of cross sections as well as infrared spectrophotometric measurements were made. The results obtained showed on the ground areas of the left part of the relief the presence of blue pigments azurite-based containing a protein binding medium partially transformed into calcium oxalate. The original blue was successively covered by a white over painting of white lead and barite. The gilded robe of the Announce Virgin is formed by a preparation layer containing minium in oil medium. The gilded layer was partially covered by a white over painting of the same composition as before observed on the ground. The internal side of the robe was painted by using copper resinate which was faded into brown colour due to photochemical decomposition. A second malachite-based layer was overlapping the copper resinate. As regards gilding technique the gold leaf is applied on a oleo-resin white lead layer. In the architectonic geometrical frame decorations of the funerary monument some re-gildings were observed.

INTRODUCTION
The artefact considered in this paper is a marble funerary monument which was originally painted.

The XIV century funerary monument of *Avoscano* family, located in the crypt of the Belluno Cathedral, was carved in marble and represents the *Announce Virgin* (right part), the *Virgin and Child* (in the middle) and the *Announcing Angel* (left part) (Vizzuti F., 1995). The actual feature is the result of the reassembling after the partial destruction of the church due to the 1873 earthquake (Fig. 1) (Spiazzi A.M. et al., 2004). Preliminary investigations included a careful mapping of the various forms of alteration affecting the marble surface of the monument primarily to study the causes of alteration and consequently to adopt the appropriate methodology for the removal of deterioration products without damaging the marble substrate.

The presence of small traces of colours appearing after a careful observation has convinced us to start an investigation to try to reconstruct the original feature of the monument (Fassina V., 2000).

In particular, we decided to investigate on the painting technique by identifying the composition of painted layers to distinguish the original areas from the re-painted ones.

In the field of analytical research applied to cultural property there is an increase in the use of instruments and techniques which aim at the minimum damage to the investigated artefacts.

Figure 1. Belluno Cathedral, general view of the Arca Avoscano.

To have a complete investigation about the painting technique an exhaustive study by comparing the results obtained by a XRF portable instrument with those obtained by the traditional micro-destructive cross-section analysis was carried out. The XRF technique is a very useful tool as a preliminary investigation and can be powerful in case of simple systems. Furthermore it is very precious when sampling is causing the loosing of significant amount of artwork. In our case in order to minimize the number of samples for micro-destructive analysis a previous screening with a portable XRF instrument was carried out. On the other side the synergic use of two recent tools ESEM/EDS, Microscope Fourier Transform Infra-Red spectroscopy (μFTIR), when used together with micro ATR device often permits the examination of very small samples without destroying them, giving detailed structural information that, for the ESEM/EDS, can determine quantitatively all the elements starting from boron (Fassina V., 1999) . Non-destructive analysis is guaranteed, for ESEM/EDS and the microATR, by the possibility of examining a specimen as it is, without particular preparation. This allows to analyze the same specimen many times, in order to obtain more and more accurate information.

EXPERIMENTAL PART

To assess the different alteration products as well as the painting techniques the following analytical methods were used:

1. Optical Microscopy (OM) of cross-sections to identify the different painting layers.
2. Environmental Scanning Electron Microscopy (ESEM) providing morphological information on crystals of the compounds.
3. Energy Dispersive Spectrometry (EDS) for achieving elemental analysis as well as the elemental distribution.

The cross sections have been realized by including the fragments with all the layers in a cold polymerizable resin.

Cross-section examination was carried out to know the layer composition and succession, under an optical microscope in visible and ultraviolet (UV) light, and by means of ESEM with EDS microprobe. Stratigraphic investigations were supplemented with specific micro-analytical tests that were carried out directly on cross-section.

RESULTS

XRF analysis and sampling collection were carried on the most significant areas and the results obtained are discussed.

The actual feature of the surface of the small columns is characterized by a non-homogeneous gilding which is alternating with some red spots (Fig. 2). The XRF analysis on the red areas shows the presence of lead which probably is ascribed to minium. Any further interpretation is not possible by XRF analysis and for this reason a cross-section optical microscopic observation was carried out on a small sample. From cross-section analysis, in contact with marble surface an orange layer of minium-based is visible (Fig. 3). Above this original orange layer there is a white one mainly lead white-based embedded in an oil medium and containing large particles of barite, barium and sulphur were identified by EDS microanalysis. Barite is a marker to date that this a repainting layer. Finally a thin gold lamina is observed.

The robe of the *Announce Virgin* presented the same feature of the column previously analyzed and the optical microscopic observations of cross section confirm the same stratigraphy.

Figure 2. Basement of the column on the left side of the left panel. Missing gilding layer showed the behind red preparation layer.

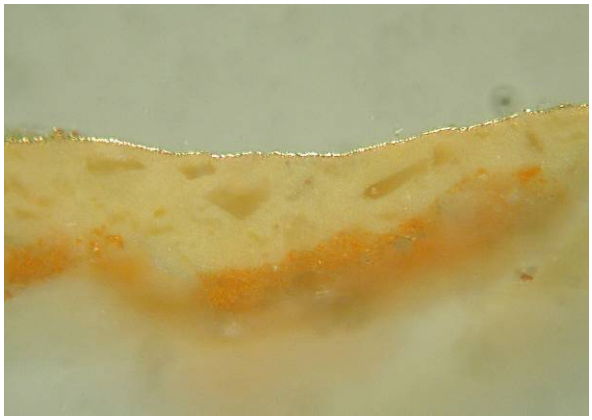

Figure 3. Cross section of the gilded layer from the basement of the column. The top gilded layer was applied on a white lead containing barite particles which are a marker of not original gold application.

Some different features, visible at naked eye on the robe, in correspondence to the shoulder of the *Announce Virgin*, were analyzed and the stratigraphies observed were a little bit different showing a very thin white lead-based in proteinaceous medium in contact with the marble. Above the preparation layer for the gold lamina there is an orange coloured white and red lead-based.

This stratigraphy probably looks like the original one because the gold lamina is directly applied above the orange red lead which was the preparation layer for the gilding as traditionally used in XIV century (Cennino Cennini, 2004). All the stratigraphies studied show a white lead layer above the orange one, probably applied after the missing of the original gold lamina and as preparation for the new re-gilding. It is not reasonable and understandable the application of the gold lamina above a white lead preparation layer, because it is not fitting with the dark ground usually used by painters to have a saturated and warm colour for the nearly transparent thin gold lamina (Thompson, 1932 & 1936).

From the internal side of the robe of the *Announce Virgin* (Fig. 4) the green colour feature is composed by a copper resinate layer showing the internal side, in contact with the marble,

completely turned into brown as a result of photochemical decomposition (Gettens & Stout, 1942), while the upper layer is still green, due to small malachite particles, even if the matrix is fading into brown (Fig. 5).

Figure 4. From the internal side of the robe of the Announce Virgin.

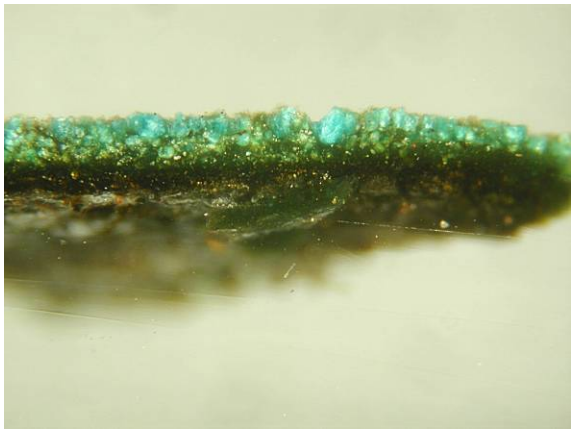

Figure 5. Cross section of green colour. The layer in contact with marble is copper resinate-based and was completely turned into brown as photochemical decomposition result. The top layer is malachite-based embedded in organic medium completely turned into brown.

The external layer is completely formed by large malachite crystals embedded in slightly brownish matrix. The malachite is an over painting probably to renew the green which was turned into brown since the beginning above the original application of the copper resinate.

The red lips of the *Announcing Angel* were analyzed by the portable XRF equipment and the presence of mercury and phosphorous is indicating the cinnabar mineral embedded in a protein-based medium.

The ground of the relief near the head of *Announcing Angel* at the border of the aureole showed a white blue feature (Fig. 6). The XRF analysis shows the presence of copper and consequently the blue colour is ascribed to azurite. The cross-section analysis shows a stratigraphy indicating that the original azurite layer (*b)* (120-270 µm) was successively covered by a thick white lead layer *(d)* (Fig. 7) containing a few barite particles thus indicating an over painting probably applied after the earthquake occurred in the third quarter of XIX century. Some azurite particles are transformed into malachite and the proteinaceous binding is turned into brown and it is partially transformed into calcium oxalate.

Figure 6. From the ground of the relief near the Announcing Angel.

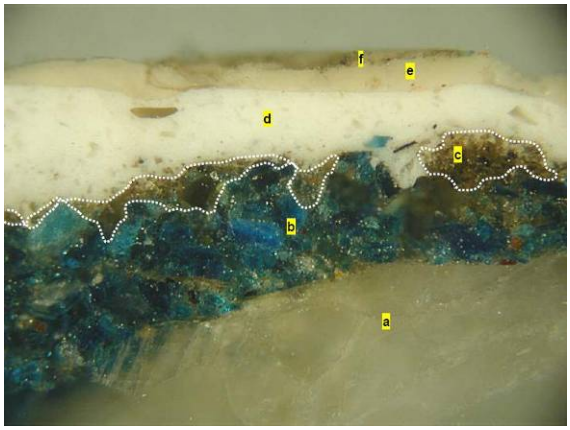

*Figure 7. The azurite pigment (layer b) is embedded in a proteinaceous binding brown coloured (layer **c**) and almost completely transformed into calcium oxalate.*

The binding material of the white lead layer is oil-based. Above the white lead layer a second white layer containing a mixture of calcium carbonate and white lead (Fig. 8) embedded in oil-proteinaceous binding determined by the presence of high amount of nitrogen and phosphorous detected by EDS analysis (Figs. 9, 10).

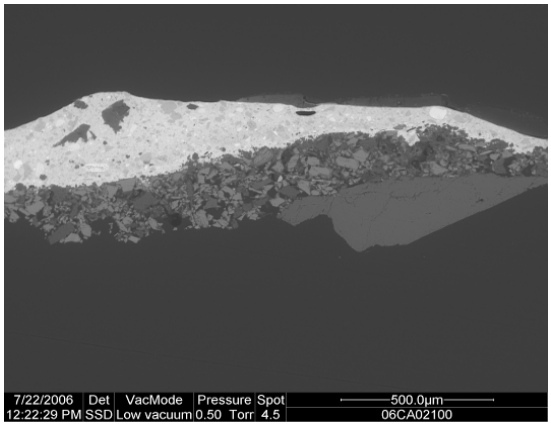

Figure 8. At ESEM-BSE the contrast between the white lead-based layer applied on the original dark azurite layer is clearly visible.

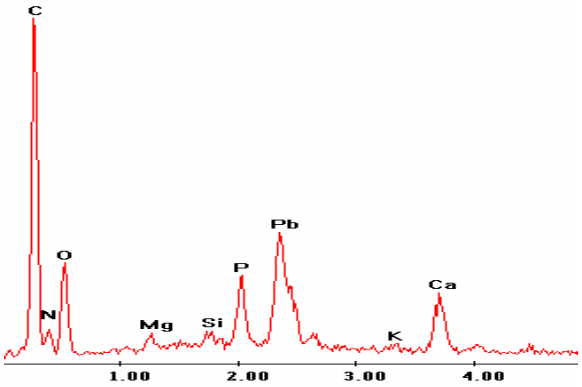

Figure 9. EDS microanalysis of the external layer shows the presence of nitrogen and phosphorous.

The cross section observation of a sample taken from the dark dentil of the superior architectural frame shows the presence of dark blue large azurite crystals embedded in phosphorous-enriched brown particles due to the protein-based medium. The actual dark blue feature is the result of the transformation of the protein medium (Fig. 11).

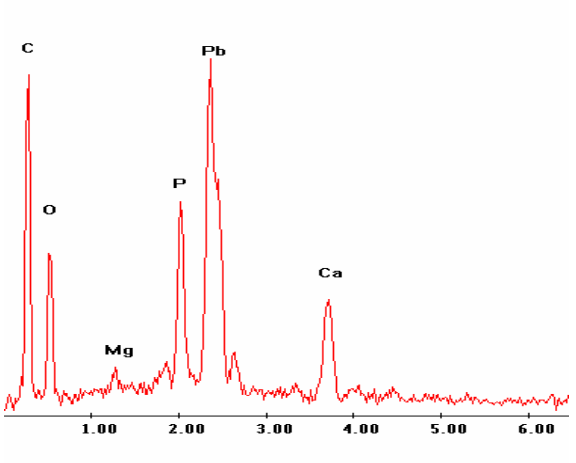

Figure 10. EDS microanalysis of the externallayer shows the presence of phosphorous.

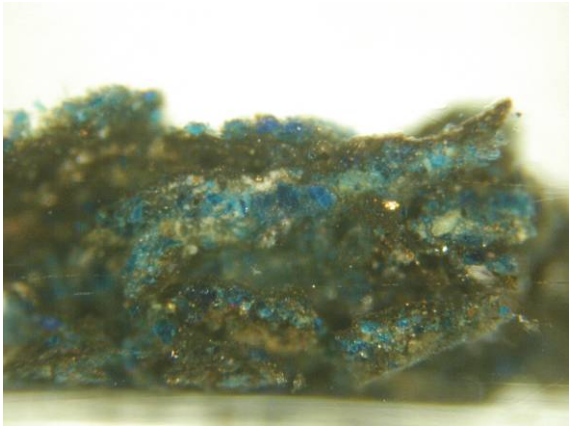

Figure 11. Cross section from the dentil of the superior freeze of the frame. Azurite pigment embedded in organic medium turned into brown.

On the edge of the architectural frame of the *Virgin and Child* relief many painted layers seem to be present (Fig. 12). The optical microscopic observation associated with FTIR analysis of red fragments show a first layer containing very fine minium particles embedded in an oil-protein-based medium used as a ground preparation for the gold lamina (Fig. 13).

Figure 12. From the edge of the superior architectural frame of the Virgin and Child central relief.

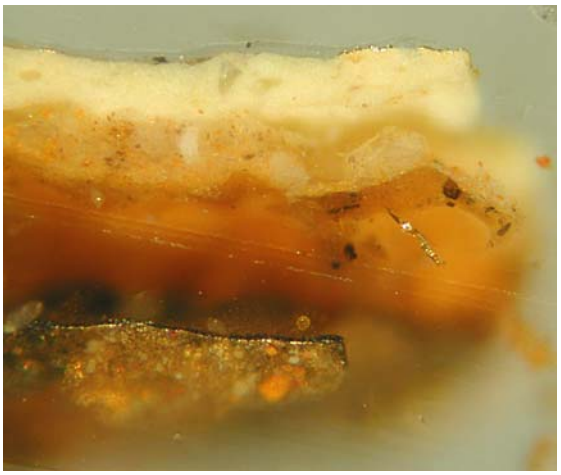

Figure 13. Cross section showing the original gold lamina (lower part of the picture) covered by a first silver lamina, turned into brown, and a second very recent gold lamina on the top.

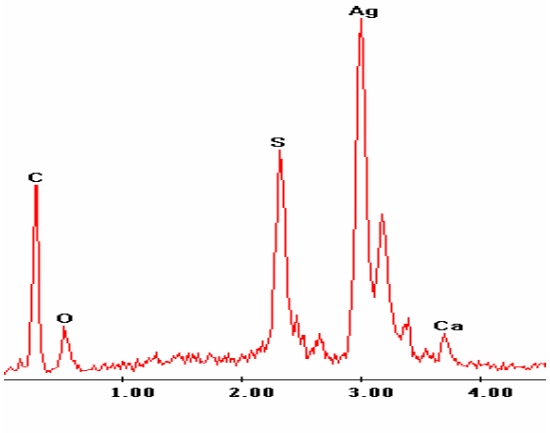

Figure 14. EDS microanalysis showing the original silver turned into the dark silver sulphide.

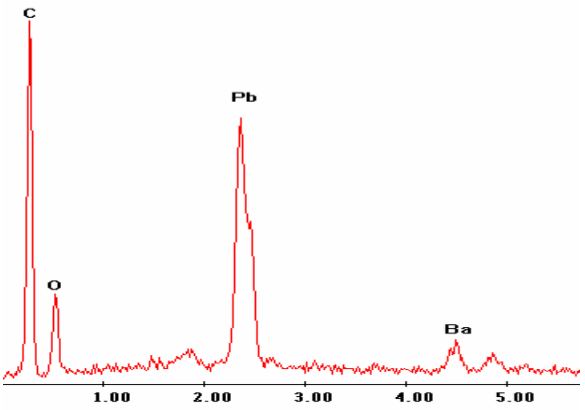

Figure 15. EDS microanalysis of the white lead repainted layer.

Surprising on the gold lamina the presence of a very thick silver lamina, completely turnished into black, has been observed (Fig. 14). Above there is a sequence of three layers: an orange organic oil-based layer is covered by an orange white lead containing a few small minium and barite particles, and then a white lead layer with a few barite particles (Fig. 15). Some remains of gold lamina were visible above these three layers.

Another sample taken from the frame of the *Virgin and Child* relief (Fig. 16) shows probably the complete stratigraphy in which three gilded layers were observed (Fig. 17). The first is a preparation layer for the gold lamina containing a few minium particles embedded in oil medium. Above the original gold (Fig. 18) a completely darked silver lamina (Fig. 19) is in turn covered by a second gold lamina (Fig. 20). Above a mixture of white and red lead and a few barite particles embedded in oil medium are visible. Above a preparation layer for the third gold lamina is white lead and barite-based (Fig. 21). Finally, above the third gold lamina, a white layer calcium carbonate and white lead-based is visible. The third gold lamina was probably renewed after the 1873 earthquake.

Figure 16. From the edge of the superior architectural frame of the Virgin and Child central relief.

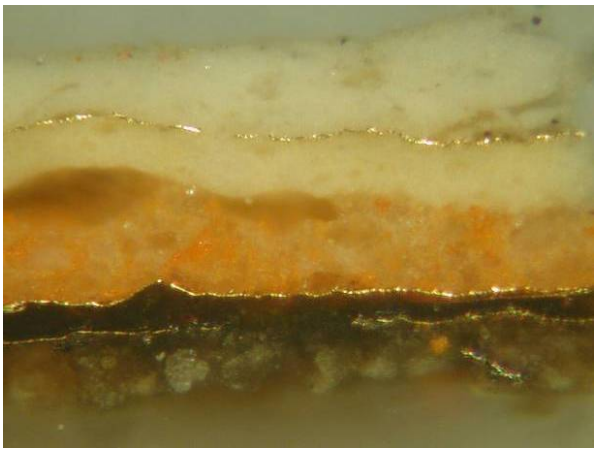

Figure 17. Cross section showing the sequence of three gold laminae and a silver lamina (turned into black silver sulphide), in between the first and the second gold lamina.

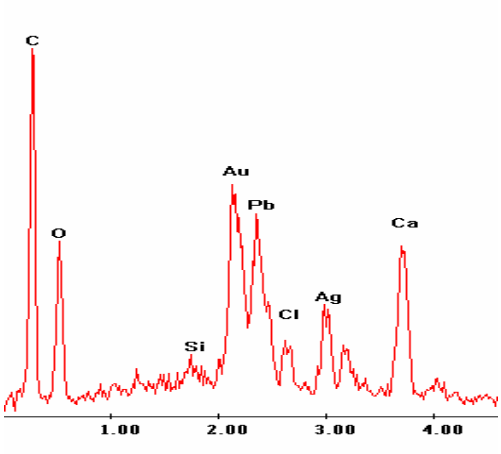

*Figure 18. EDS microanalysis of the original gold lamina (layer **b**).*

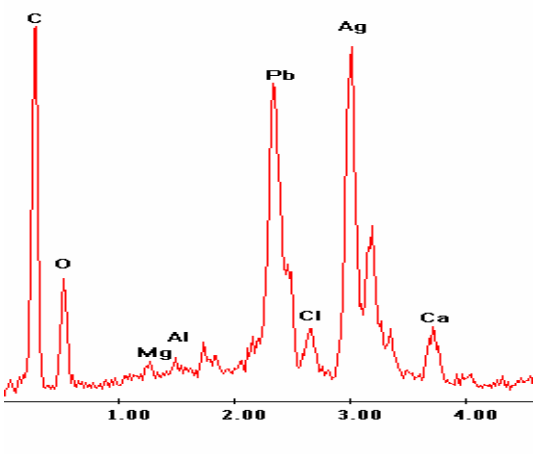

*Figure 19. EDS microanalysis of the silver lamina (layer **c**)*

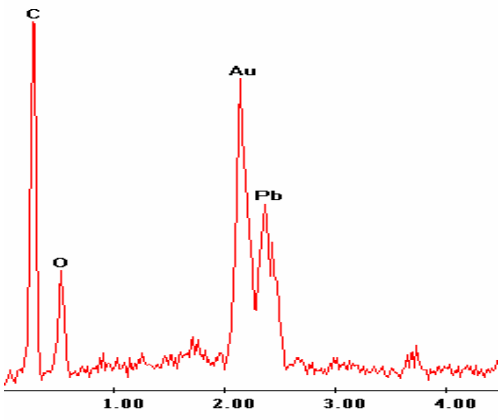

*Figure 20. EDS analysis of the second gold lamina (layer **e**)*

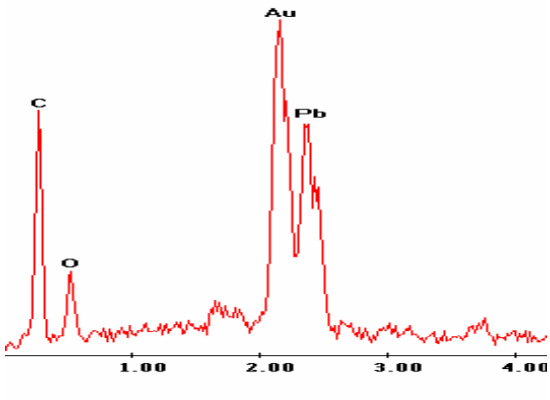

*Figure 21. EDS microanalysis of the third gold lamina (layer **h**)*

Comparison of these last two samples indicates that the first one is missing some layers and we can say that the frame was originally gilded by applying gold above an orange preparation layer minium-based. The same gilding technique was used for the robe of the *Announce*

Virgin and the columns. On the contrary to the other gilded areas, in this case the second re-gilding is obtained by first applying a silver lamina followed by the gold one and this intervention is ascribed to a period before the last re-gilding.

The application of the orange and white layer, as preparation for the third re-gilding, is coeval to the white layer used in other areas probably after the above mentioned church reconstruction in the occasion of the 1873 earthquake.

On the side of the throne some red colour traces were analyzed and a red layer containing small particles of vermilion was applied above a white glue layer with few amount of gypsum as preparation layer.

The surprising missing of painted layers on the central part of the *Virgin and Child* relief is strongly in contrast with the remains of painted colours on the superior frame as well as on the other panels of the relief and the most probable hypothesis is the intentional removal of painting not easily understandable.

To this purpose two samples of surface treatments were taken by using pads of acetone to identify organic substances extracted from the surface. The FTIR analysis shows the presence of wax and oil probably due to maintenance operations.

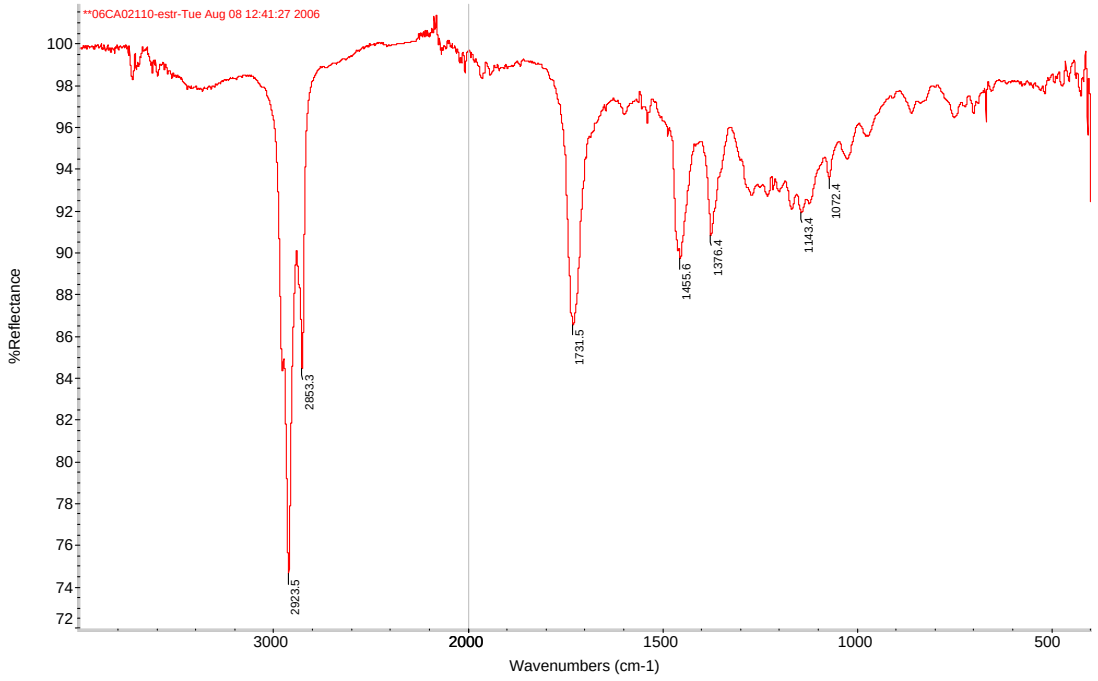

Fig. 22. FTIR spectrum of acetone sample extracted from the surface.

CONCLUSION

A careful observation of the funerary monument surfaces showed the presence of some remains of coloured layers on the marble surface of the relief.

After preliminary investigations with a XRF portable instrument a more detailed study by using ESEM/EDS allowed us to identify the colours and their original stratigraphy.

Very limited areas presented the original gilding stratigraphy obtained by the application of a gold lamina above an orange-red minium-oil-based preparation layer which is in direct contact with the marble. On the contrary, extensive areas showing gilding layers applied above a white lead preparation layer containing barite particles were not considered original due to this different technique of application. In particular, on the superior architectural frame of the relief an intermediate silver lamina, completely turned into brown, followed by a second gold lamina was applied, in a period not identified, but surely before the last re-gilding occurred after the church reconstruction in the occasion of the 1873 earthquake.

The re-gildings of the frame confirm the frequent maintenance that was done on the relief.

The original blue ground areas of the left part of the relief was originally azurite-based and the protein binding medium has turned into brown as it is clearly visible under the optical microscope (Fig. 7). The µFTIR analysis showed the presence of significant amount of calcium oxalate due to the transformation of the organic medium.

The original blue of the ground, as well as the missing gilding of the columns and flowers, were partially covered by a white over painting white lead-based. The presence of a few barite particles is a marker for dating this intervention in the occasion of the church reconstruction after the 1873 earthquake.

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