UNIVERSITÀ DELLA CALABRIA

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Dipartimento di FISICA

Scuola di Dottorato

SCIENZEA E TECNICA "BERNARDINO TELESIO"

Indirizzo

FISICA

MATERIALI MOLECOLARI E MESOFASI

CICLO

XXVII

NEW METHODS FOR CHARACTERIZATION AND DATING IN MATERIAL OF CULTURAL HERITAGE

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NEW METHODS FOR CHARACTERIZATION AND DATING IN MATERIAL OF CULTURAL HERITAGE

1. Introduction

Scientific investigation of the state of conservation of historical and artistic heritage is now a basic need of both the cognitive processes of the works and for the proper preparation of the conservation work conservativi. In particular, diagnostics, analyzes the changes in the structure and constituent materials of the object produced by the degradation, identifies the causes, identify the most appropriate solutions to stop or mitigate the effects of the processes of deterioration. At the same time the analysis of materials can lead to define the age of the haritage. The Scientific analysis of artefacts opens the lines of research aimed at the achievement of an observation method that overcomes the limitations of the human eye and allow to look at the work of art in the smallest details, even within his structure.

My PHD research project aimed to developed diagnostic methods for the characterization and dating of cultural heritages, the non-destructive methods have been used where it was possible, that have given reserchers in the fields of art conservation the opportunity to study many of materials encountered with greater and flexibility than ever before.

I report in the following paragraphs the list of my researches made on this field, fivecase studies that have made an important contribution to the research and planning for restoration of cultural heritage.

2. New methods for characterization and dating in wooden material of cultural heritage

2.1 Scope

Iimprove the spectroscopic technique with respect to the following directions :

- IR characterization of the main types of wood used in the production of works of art
- Study of the effect of aging of different types of wood by means of IR spectroscopy, resulted from light and moisture
- Application of FTIR microspectroscopy for the study of the spectral profiles of depth in order to develop a new method of dating.

This study will focus on the change in the chemical composition of old wood, because of physical, chemical and biological processes found in the IR spectrum, an area of particular interest is that between 1200 cm -1 and 1300 cm -1. Once identified by the reading of the spectrum the type of essence, it necessary to compare the spectrum obtained with spectra of wood of the same type ofessence, of known age. On this basis, we can express a reliable dating

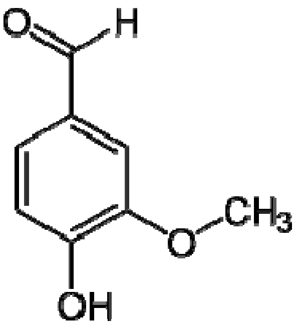
2.2 Introduction

The main components of wood are cellulose and hemicellulose (both polysaccharides but with different structures and molecular weight), lignin (polymerized derivatives of phenylpropane), H2O (percentage of which varies with the degree of curing) and various other substances including resins. Among the different types of wood there are obviously differences in the chemical composition, for which the study of the absorption spectra IR allows an identification of the type of essences. When the wood aging changes because of chemical, physical and biological, changes the chemical composition of wood.This study is focused on the change in the composition that is also found in the IR spectrum. The absorption frequencies moving and the intensities of the peaks vary. An area of particular interest to this method is that between 1200 cm-1 and 1300 cm-1.

The dating for comparison may be possible because, while the outer layer essentially decomposes rapidly to climatic factors, the inner part of the wood undergoes a slow and steady chemical degradation The various species in the continents during the aging would have the same decay, except for the tropical climate countries (Equatorial Africa, Southeast Asia, etc.) and in regions with long periods with temperatures below the freezing point (Canada, Finland, etc.) . So, with the exception of extreme weather areas, the trend of chemical decay for a specific family or species of trees would be independent of the location, and then, for all climatic zones medium would suffice, the same database with reference spectra of different types of wood for a date with the spectroscopic method.

2.3 Main objectives

With this work we want to experiment and to propose an innovative method of dating based on quantitative analysis of the degradation of certain functional groups, in particular the carbonyl group (C = O) of lignin, belonging to the molecules of the wood. cellulose remains stable in time and does not undergo appreciable degradation processes, unless it is maintained in conditions of high temperature, high humidity or high impact radiative. The lignin has a rather instability significantly higher. The instability may be due either to the loss of volatile aldehyde groups (for example, vanillin) (see picture1) that in slow oxidation processes.



p.1 vanillin

Both processes lead to a variation of the amount of carbonyl groups present on lignin, unless one does not compensate for the other. The loss of vanillin leads to a decrease of carbonyl groups while the oxidation leads to their increased. On the other hand, the carbonyl group absorbs, with high quantum yield, infrared radiation,for stretching vibration, at a frequency centered around 1725 cm-1 The focus was therefore on temporal evolution of this transition to try to correlate the intensity of the age of the wood. The strategy of work has provided for the selection of a number of antique sculptures and wooden artefacts whose dating was certain, at least relatively to the century of realization, and perform FTIR analysis, non-destructive, on portions not protected by paint, once found their perfect integrity in terms of morphological and biochemical. At present it has been possible to identify a small number of samples. The choice of samples, responds, for the moment, two different needs. The first concerns the fact that you can have multiple samples of the same type of wood belonging to different historical periods (samples of poplar, walnut and pine dating XV-XX century). Another requirement is to verify if wood of different nature behave in a different way.

2.4 Research Activity and Results

The analyzes were carried out on a series of 19 samples, poplar, walnut and pine, from wooden sculptures of churches in: Paola (CS): church of SS Rosary, Church of St. Mary of the Assumption, St. James, the Cathedral and the church of St. Michael, and from Laurignano (Cs): Sanctuary of the Blessed Virgin Mary of theChain.

The analyzes were carried out using the sample in situ, without sample pretreatment. The spectra were obtained in absorbance by means of a FTIR spectrometer Alpha Art Conservation (Bruker) in the range between 4000 and 400 cm-1, mediating 47 scans for each sample.

To discuss the changes induced by the passage of time in the IR spectrum of the wood, it is considered mainly signals that fall between 1800 and 1700 cm -1, which correspond to the stretching vibration of the carbonyl. The amount of these groupings within the lignin may change especially for oxidation induced by oxygen of the air (in the presence of light) for attack on the residual double bond soft he lignin.

They are, therefore, taken into account the integrals subtended by the bands related to the absorption of the carbonyl groups (C = O), between 1775 and 1700 cm-1.

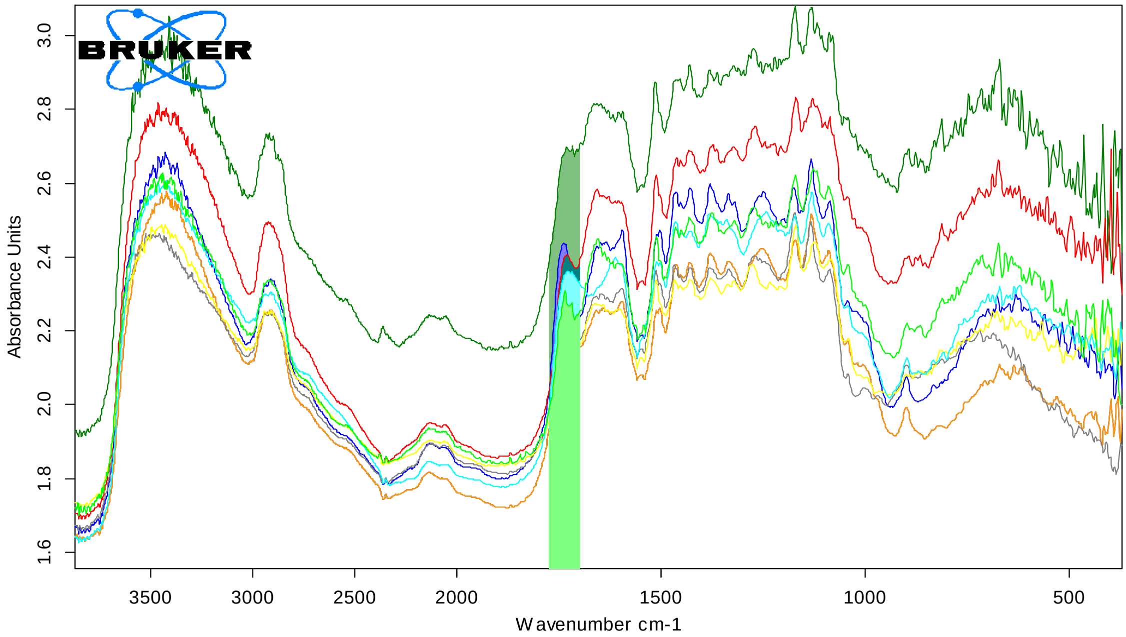
However, the intensity of the radiation reflected by the sample, measured by the spectrophotometer used in reflection, depends not only by the absorption of the sample, but also by factors geometric positioning of the sample with respect to the incident radiation. has been explored the possibility that it could be significant, for the purposes of dating of wood, the ratio of the integral of the spectral transitions regarding the area of absorption of different carbonyl groups (aldehydes, ketones, carboxylic acids and esters) and the entire area spectrum between 1700 and 1000 cm-1 band comprising mainly the absorption of the aromatic rings, the bending of the methylene and methyl groups. The uncontrollable effect of geometric factors that certainly influence the absolute value of the intensity of the spettral lines in this report should be eliminated.

All the spectra of the lignin present a very intense band between 3500 and 3000 cm -1 assigned to the stretching vibration of-the-OH. This band is caused by the presence of alcoholic and phenolic hydroxyl groups that are involved in hydrogen bonds. The intensity of the band increases with the demethylation of the methoxyl groups present on the third or fifth carbon of the aromatic ring that are expelled and replaced by H atoms to form new groups -OH; decreases with the inverse process, the methylation of -OH, which provides for the expulsion of H to be replaced by methyl groups. This band (not considered useful for the dating of the wood) is not analyzed in this study because in this range are affected the absorption of water that is not in a percentage finely controllable.

It is further noticed that the area of the finger prints (between 1000 and 400 cm-1) is affected in a relevant way of drifting problems of spectral line of the base. For this reason it was chosen to use as the reference spectral area between 1700 and 1000cm-1.

Shown below are the results of the samples respectively to essence

Essence of Poplar.



pict.2 e 3

🟩 Madonna Assunta Base

🟦 Madonna con Bambino (capelli)

🟨 Madonna con Bambino (Rosario-base)

🟥 Madonna con Bambino (base)

⬜ Madonna della Catena

🟦 Madonna della Catena con Bambino

🟧 Madonna della Catena con Bambino (base)

🟪 Madonna in trono con Bambino

🟩 S. Francesco

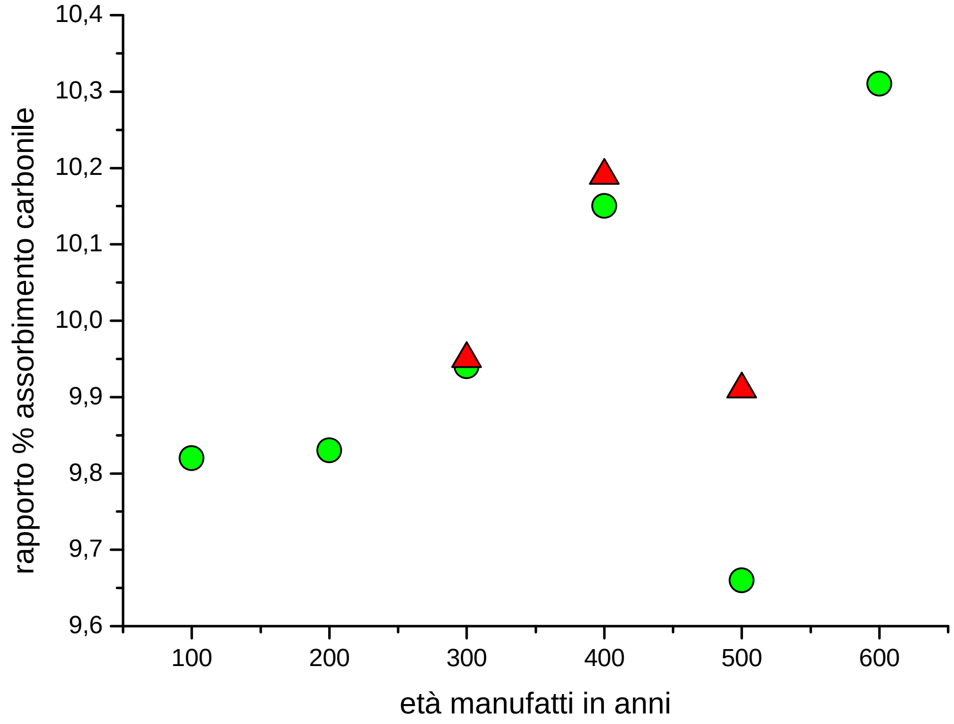
In pictres 4 and 5: Regions IR spectrum expressed in absorbance. The spectra of the samples in poplar, highlight the areas under the integrals, respectively: 1775-1700 cm -1 and 1700-1000 cm-1.

Campione	**Integrale *C=O* 1775-1700cm^{-1}**	**Integrale 1700-1000 cm^{-1}**	**Valutazione percentuale**	**Datazione**
Madonna in trono con Bambino	169.5	1643.5	10.31%	XV
Madonna con Bambino (Rosario-base)	158.697	1601.111	9.91%	XVI
Madonna Assunta Base	165.011	1706.720	9.66%	XVI
Madonna della Catena con Bambino (base originale)	150.4	1476.8	10.19%	XVII
Madonna della Catena	156.5	1542.6	10.15%	XVII

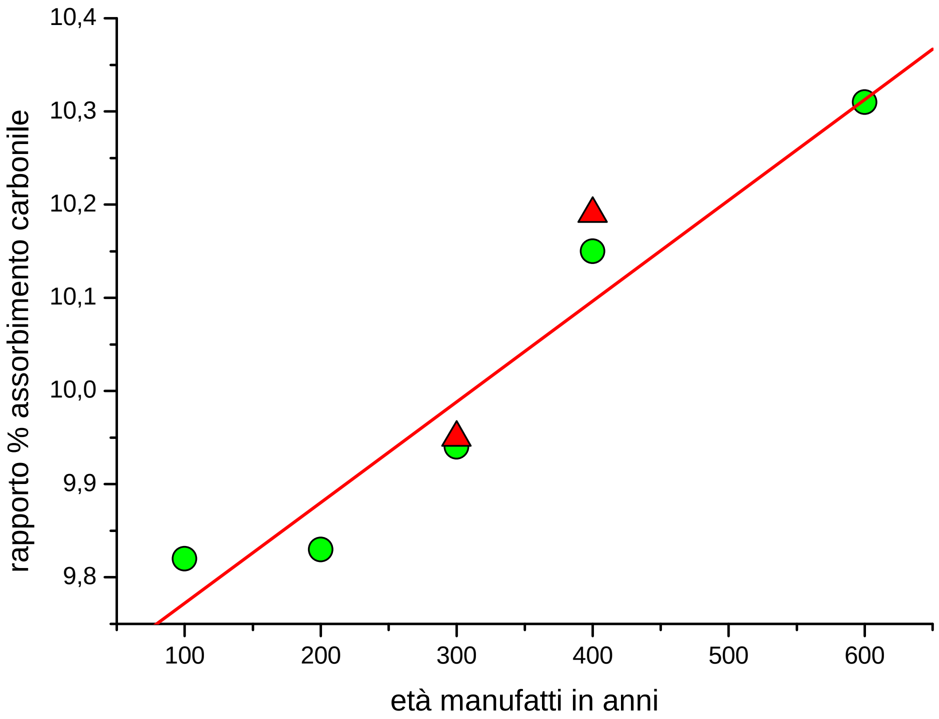
Madonna con Bambino (base)	170.6	1715.9	9.95%	XVIII
Madonna con Bambino (capelli)	164.07	1659.3	9.94%	XVIII
S. Francesco	196.242	1995.521	9.83%	XIX
Madonna della Catena con Bambino	164.3	1652.0	9.82%	XX

Tab. 1: Sample data in poplar

By analyzing the same type of woodit is possible to see that the overall standard of the absorption band of the carbonyl tends to increase gradually with increasing age of the wood. The data are more easily assessable in the subsequent figure 4, in which the normalized absorption of the carbonyl band is reported as a function of time.



pict.5

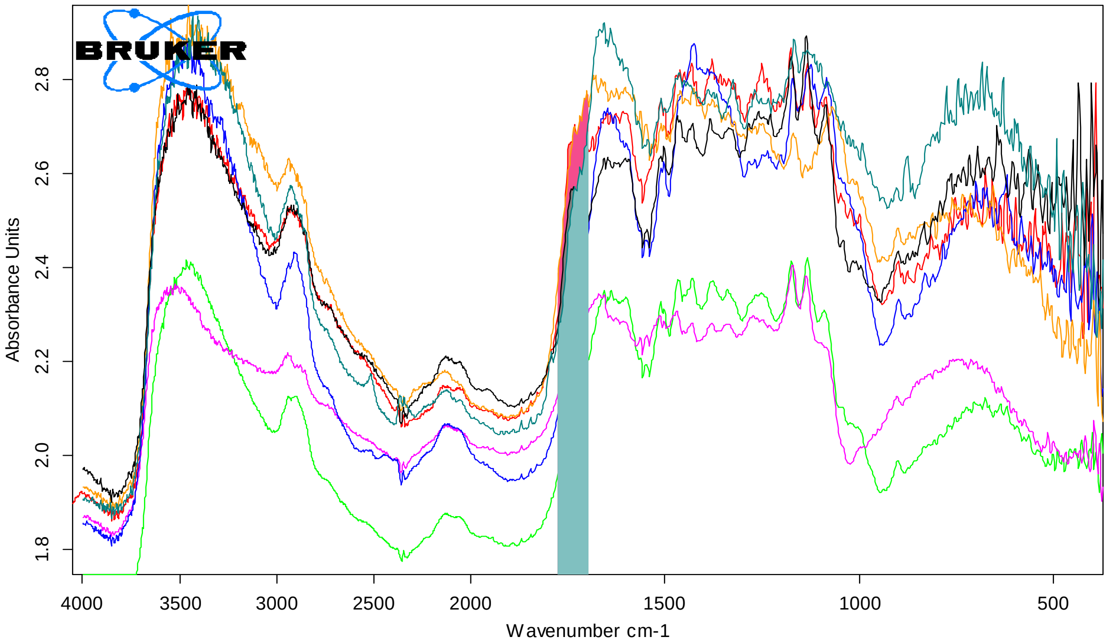


pict. 6

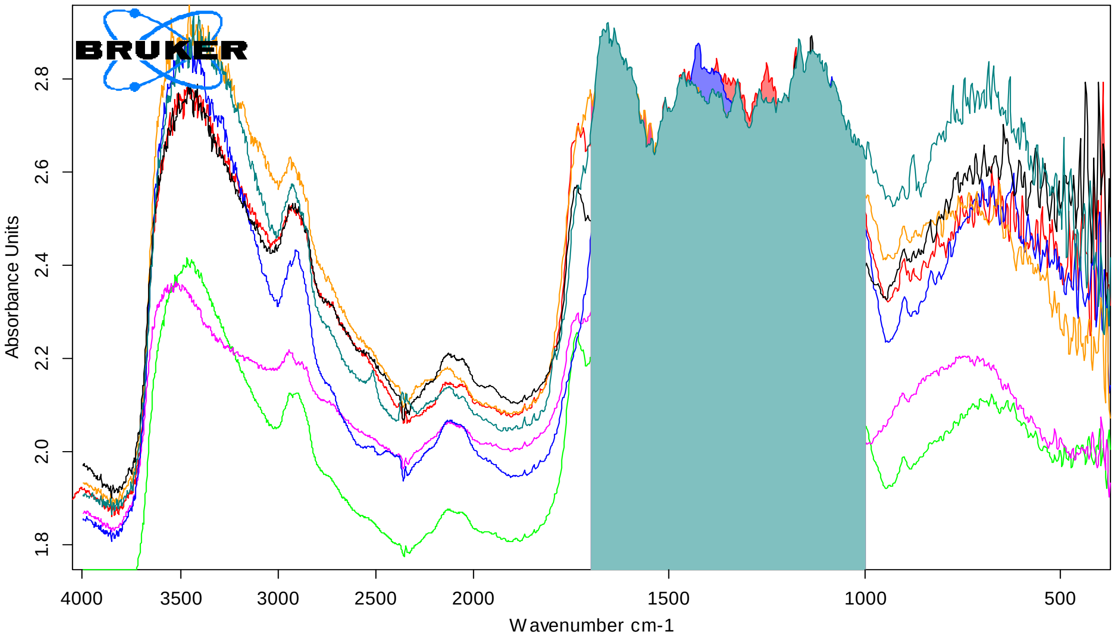
Fig.5 e 6 Evolution of the normalized integral of the absorption band of the carbonyl in the FTIR spectra of poplar wood on the age of the wood.

As it possible to see, the points representing the "Madonna and Child (Rosario-based)" sample placed in the church of SS. Rosary in Paola (CS), and the "Lady of the Assumption (base)" sample placed in the church of St. Mary of the Assumption and St. James the Less in Paola (CS), respectively, 9.91% and 9.66% in the ratio, discard a lot compared to the trend of the other points. Excluding these two points, as shown in the second graph (Figure 6), we obtain a good linear correlation with standard deviation (R = 0.9722). The possible reason of the difference of the high points eliminated it was thought that the possible cause of deviation from the trend may be due to the fact that the samples analyzed in these two cases correspond to points of the base of the statues. This choice was made to avoid the presence of contaminants used to protect and strengthen the wood during the restoration.

Essence of Walnut



pict7



pict8

9

■ Confessionale Duomo

⬛ Confessionale Rosario

🟧 Coro Base Duomo

🟦 Coro Duomo

🟥 Confessionale S. Giacomo

🟪 Sagrestia Base Duomo

🟩 Sagrestia Duomo

In Figures 8 and 9: Regions IR spectrum expressed in absorbance. The spectra of the samples in walnut, highlight the areas under the integrals, respectively: 1775-1700 cm -1 and 1700-1000 cm-1

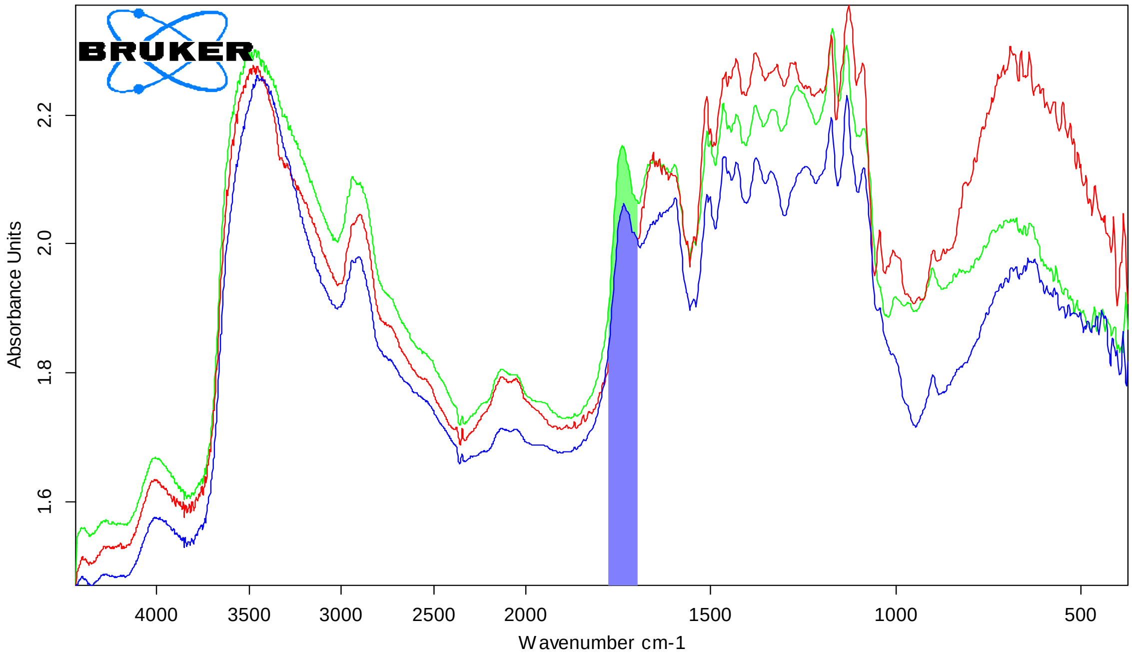
Before discussing the data obtained for this kind of timber, it should be emphasized that in this case the essences investigated are all of the same century. The reason that we proceeded to the analysis is connected to the possibility to analyze the variability of the comparison data used here, in case the time of date of the work is identical.

Campione	**Integrale *C=O* 1775-1700cm^{-1}**	**Integrale 1700-1000 cm^{-1}**	**Valutazione percentuale**	**Datazione**
Coro Base Duomo	197.282	1891.490	10.42%	XVIII
Coro Duomo	168.392	1870.203	9.00%	XVIII
Confessionale Rosario	186.816	1847.534	10.11%	XVIII
S.Giacomo Confessionale	195.227	1904.571	10.25%	XVIII
Sagrestia Base Duomo	169.273	1579.902	10.71%	XVIII
Sagrestia Duomo	162.836	1603.897	10.15%	XVIII
Confessionale Duomo	187.583	1940.169	9.66%	XIX

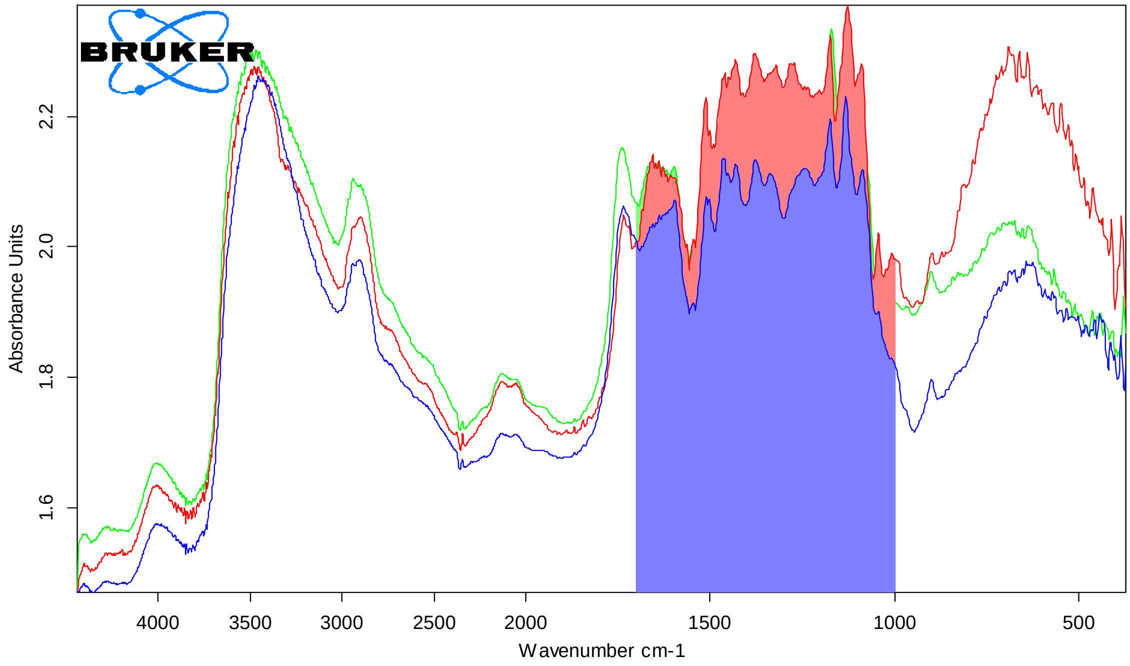
Table 2: Sample data walnut.

The data reported in Table 2 show a high variability for the various samples, although the dating is almost identical. It is not currently possible to interpret this variability. Further studies are needed to determine the spectral behavior of wood samples of this essence very different to dating. E 'possible that the lignin of the walnut is much more vulnerable than the oxidative processes compared to that of poplar. This is, however, only very preliminary hypothesis to be considered together with other plausible.

Essence of Pine.



pict. 9



pict.10

🟦 Coro Ligneo
🟥 Organo S.Giacomo
🟩 Testa manichino (collo)

In pictures 9 and 10: Regions of the spectrum IR expressed in absorbance. The spectra of the samples in pine, highlight the areas under the integrals, respectively: 1775-1700 cm -1 and 1700-1000 cm-1.

Campione	**Integrale *C=O* 1775-1700cm^{-1}**	**Integrale 1700-1000 cm^{-1}**	**Valutazione percentuale**	**Datazione**
S.Giacomo Organo	148.273	1526.585	9.71%	XIX (prob. 1819)
Testa manichino collo	172.83	1857.02	9.30%	XIX
Coro ligneo	154.04	1594.6	9.66%	XX

Table 3: Sample data of pine.

The data are grouped although there is still a variability higher than that of poplar. Even in this case, similar considerations apply to those set out above concerning the essence of woody walnut.

2.5 Conclusion

In this work, we wanted to explore the possibility of dating the wood of historical and artistic, using FTIR spectroscopy in reflection, a method that would allow the analysis of the works in situ, in a completely non-invasive. In particular, it is sought to establish whether there is a correlation between the integrated intensity of the peak of the carbonyl and the date of the work. For the elimination of uncontrollable factors due to the geometry of the samples and the positioning of the instrument with respect to the same surfaces, more than using the absolute spectral absorption of the carbonyl band was thought to use the percentage ratio of the peak area of carbonyls (1775-1700 cm-1)with the spectral area subtended between 1700 and 1000 cm-1.

In drawing conclusions, critical issues for the development of a methodology for dating are:
-for some artwork using paraloid b72 used as a hardener for the restoration catching and invalidate the results.
- The need to cross the methodology with statistical treatments that must necessarily be based on a greater number of data

3.Methods to characterize and dating ancient icons: study of two icons triptych of the Museum of Frascineto

3.1 Scope

The scope of this research was to ascertain the possibility to use optical and SEM (Electron Scanning Microscopy) to characterize and to date ancient icons. In Particular, the identification of repainting and refurbishment of two icons triptych from the Museum of Frascineto were studied. in order to plan their rastauration.

3.2 introduction

Fig.1 a) Icona Trittico Madre di Dio Odighitria (Icona A). b) Icona Trittico Madre di Dio Regina (Icona B)

The first icon under study (Fig. 1 a), the Mother of God Icon Triptych Odighitria, hereafter Icon A, is in fairly good condition. The work has been subjected to restoration (light cleaning) in recent times, probably in the late '90sWe don’t have any news about the restoration invasive that appears most evident in the central panel.

The wooden frame of the central panel shows in the bottom an area burned, which seems to extend subject of painting restoration. The icon shows an attack by insects Damaging. More details on the painted areas are obvious observation with a Wood's lamp in UV light.

The second icon under study (Figure 1 b), the Queen Mother of God Icon Triptych, from here on B Icon has never been restored and is in bad condition of conservation.The colors are altered and covered with a dirty spread, the golden parts, especially the halos are numerous falls in the paint layer and prepared ness.

The icon has a clear attack damaging insects.

3.3 Diagnostic investigation with UV lamp

The analysis in the UV light was carried out with a tool ART LUX 70 of the firm CTS srl consisting of a double UV lamp4w.

The images were acquired by a normal digital camera.

The Icon A, illuminated with UV light (Fig. 4.2), has a lot of repainting, particularly the central image shows a large area repainted.

Fig. 2. Icon A illuminated with a UV lamp

This is compatible with a restoration invasive, performed to "rectify" to an extended burn, probably originated in the lower part of the icon (Fig. 4.3 b) and which had destroyed the entire central part of the main blade, almost totally deleting the face. An example of such a "reconstruction" is the right hand of the Virgin (Figure 3 c).

A similar lack of homogeneity of the UV response there is on the cloth covering the feet of the Child Jesus (Fig. 4 a).

The Virgin's face is almost completely repainted (Fig..4 b), while the face of the Child Jesus (Fig..4 c). is adjusted to a lesser extent, the halo gets covered with glitter

Fig.3. Vergine con Bambino in luce UV. a) Parte superiore,
b) parte inferiore, c) dettaglio della mano

Fig.4. Vergine con Bambino in luce UV a) Drappo piedi del Bambinob) Volto della Vergine. c) Volto del Cristo

The upper frame of the central panel has painted areas (Figure 4 a), as well as part of the fund is on the top left and to pright (Fig.4 b c).

The area burned was not the most repainted (Figure 6 ab). The restorer has probably decided to preserve the memory simply touch up the edges.

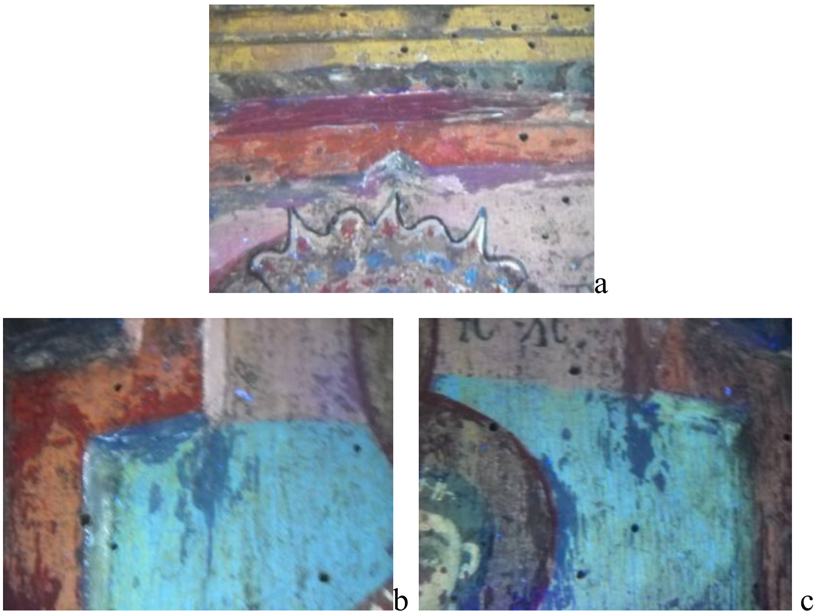


Fig.5 Dettagli della cornice della Tavola centrale dell' Icona A, in luce UV. a) Bordo superiore. b) Parte sup. sinistra. c) Parte sup. destra.

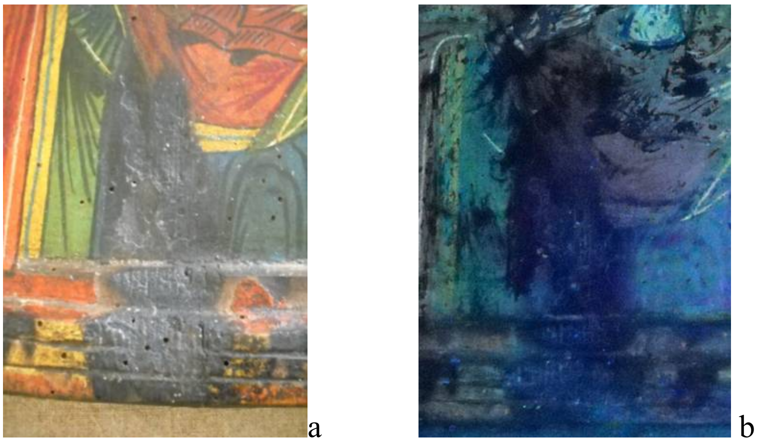


Fig.6 Area bruciata dell'Icona A. a) in luce visibile, b) in luce UV

The two side doors have been restored, St. Irene, pictured at the top of the left, has undergone alterations to the face, hand sandhalo (Fig.7).

On the image of San Charalampo, painted on the upper part of the right, it is clear a large area repainted, on the right hand and the beard (Fig.8d).

On the bottom of the left, it is possible to see repainting the face of St. George (Fig..9 c) and the repainting of the edges, especially on the left side of the painting (Figure 9 b). St. Demetrius, painted on the lower part of the right, has undergone very few repainted the face and on the horse, and has undergone a remarkable repainting the bottom edge (Fig. 10 cd).

Fig.7 Santa Irene a) Immagine nel visibile. b) Immagine nell'UV. c) dettaglio volto. d) dettaglio mani

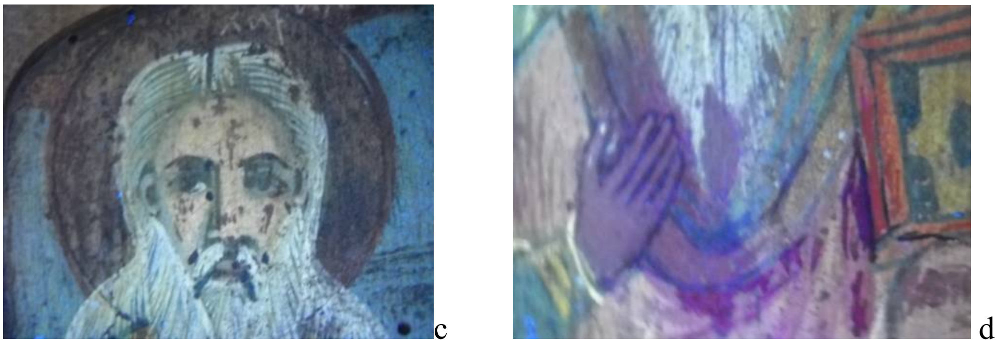


Fig 8. San Charalampo: a) Immagine nel Visibile. b) Immagine nell'UV c) Dettaglio volto. d) Dettaglio mano

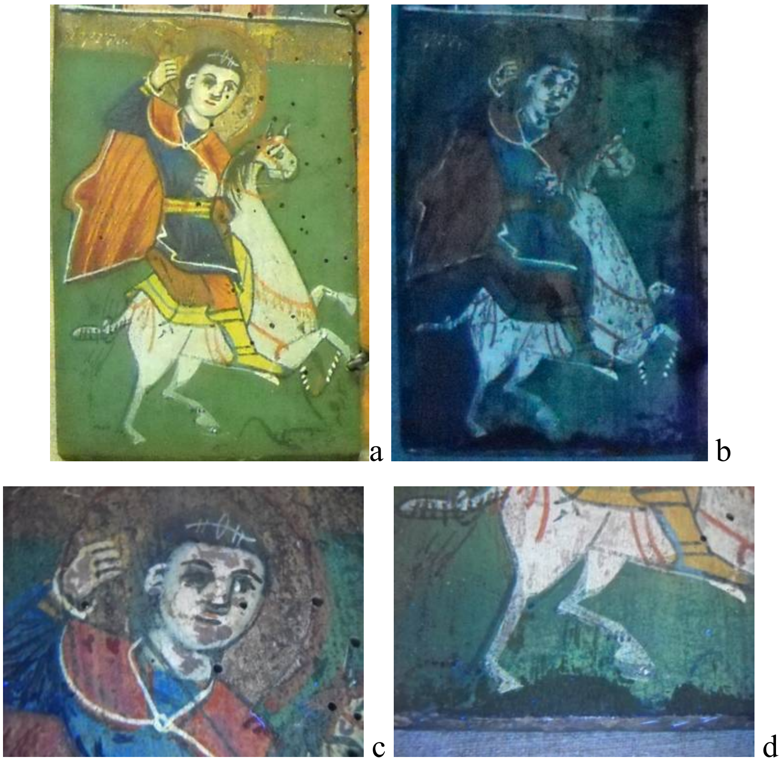


Fig.9. San Giorgio a) Immagine nel visibile. b) Immagine nell'UV c) dettaglio volto. d) dettaglio bordo inferiore

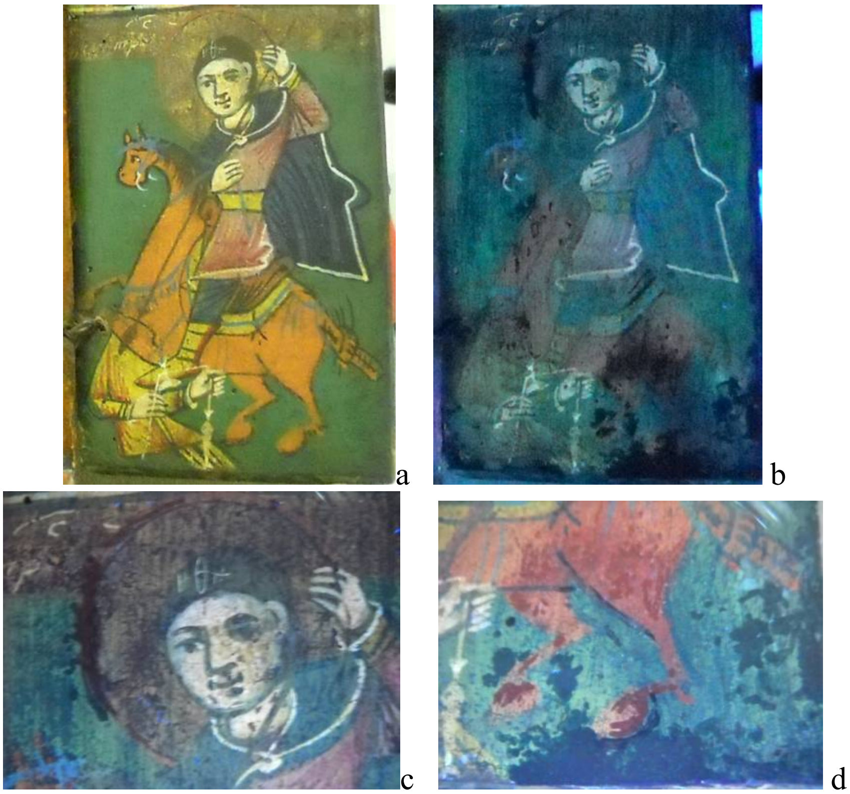
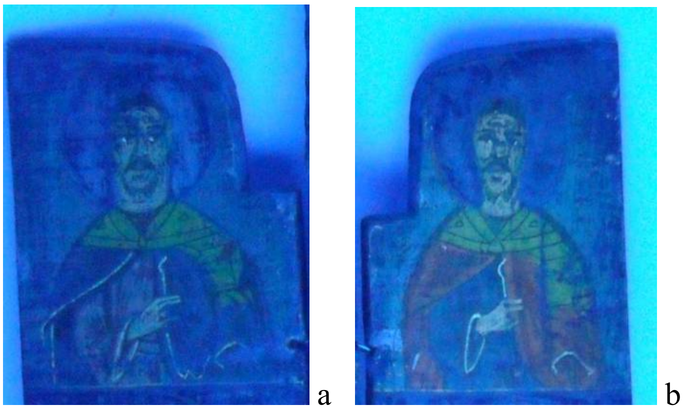


Fig.10. San Demetrio a) Immagine nel visibile. b) Immagine nell'UV.

c) Dettaglio volto. d) Dettaglio bordo inferiore del dipinto.

The Icon B, that is, one that has not undergone restoration, observed in UV light is highly reflective and gives an answer "homogeneous". This can be interpreted with the absence of repainting and new paints

Fig. 11. Icona non restaurata osservata ai raggi UV



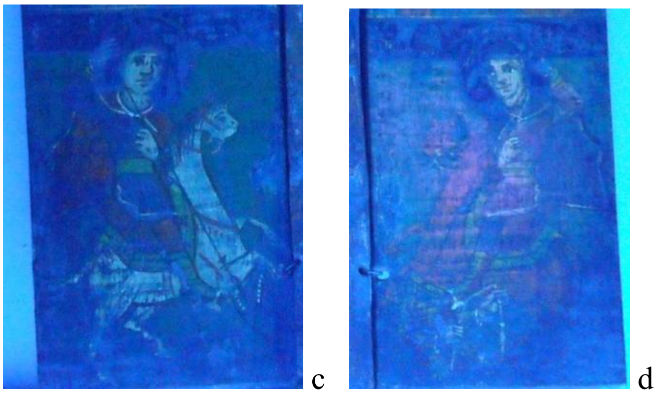


Fig. 4.12 Icona B, ingrandimenti ante laterali in luce UV

3.4 Diagnostic Survey in the near-IR(NIR).

The instrument used for the survey is a Riflettografo DG.1by Bresciani), 2 megapixels, with NIR and UV water purifier system. It is a solid state camera (CCD) connected to a personal computer, and interfaced with a software for viewing, capturing and saving images. The camera is equipped with an internal 9 filters (UV, visible, blue, green, red, NIR 1, NIR 2, 3 NIR, NIR 4) that allow you to select the band of radiation to be detected.
The bands of wavelength detectable through the filters NIR (Near Infra Red) are respectively:

•NIR 1: High-Pass Filter 750 nm.
•NIR 2: High-Pass Filter 850 nm.
•NIR 3: High-Pass Filter 950 nm.
• NIR 4: High-Pass Filter 1020 nm.

By observing in the near-IR (Fig. 4:12 b, c) did not reveal different patterns in the underlying layers,such as remorse or corrections by the author.

You may notice a different response of some parts of the picture which correspond to the painted areas, for example the hand and part of the neck of the Madonna (Fig..13), the hands of Santa Irene and San Caralampo (Fig.14 and 16) the tail of the horse of St. George (Fig. .15), the green background (Fig. 17).

Fig.12 Icona A: a) nel Visibile. b) NIR1. c) NIR2.

Fig.13 Immagine tavola centrale; Vergine con Bambino
(da sinistra Visibile; NIR1; NIR2)

Fig. 14 Anta sinistra parte superiore; Santa Irene
(da sinistra Visibile; NIR1; NIR2)

Fig. 15 Anta sinistra parte inferiore; San Giorgio
(da sinistra Visibile; NIR1; NIR2)

Fig. 16 Anta destra parte superiore; San Charalampo
(da sinistra Visibile; NIR1; NIR2)

Fig. 17 Anta destra parte inferiore; San Demetrio
(da sinistra Visibile; NIR1; NIR2)

3.6 Diagnostic investigation in raking light.

The analyzes were performed in raking light with a lamp IANIRO, Lilliput MAX 650W - 240V - G6,35; image acquisition was performed with a normal digital camera. The survey carried out in raking light at the Icon, there were many details. The face of the Virgin presents elevations, possibly to swelling of the preparatory layer or alterations of the wooden panel (Fig.18a).

On the halo of the Child can be seen lifting color and wood-boring attacks on the chest and neck (Fig. 18b).

In the middle are found cracchettature, uprisings and attacks xylophages (Fig..18 cd).

Fig.18 Luce radente Immagine centraleVergine con Bambino;
a) Dettaglio volto della Vergine; b) Dettaglio volto del Cristo;
c-d) Dettaglio parte centrale Vergine con Bambino

A light grazing the burned area can be seen very clearly, it shows the extent of the damage that has affected the paint, the paint layer, preparation and wooden panel (Figure 19). On many parts of the icon are the depressions that provide information on the restoration of the paint layer that was made without fillings.

Saint Irene painted at the top of the left has lifting and peeling of the paint film on the left hand (Fig. 20 d), after re-painted and loss of color also on the halo (Fig. .20 B). attack by wood-boring insects on the lower part of the image (Figure 20 C). Note also the incision made by the artist to delineate the halo (Fig. 20b).

On the image of San Charalampo are chipping of the paint surface preparation in the middle attacks and wood-boring insects in the lower part (Fig. 21). Very clear engraving executed by halo (Figure 21b).

The image of St. George (Fig..22 a) is badly damaged from attack by wood-boring insects, with small loss of color and lifting the halo; the image of St. Demetrius (Fig. 22 b) does not have any particular problems. On both figures we see the engraving of the halo.

Fig. 4.19 Zona bruciata dell’Icona A osservata in luce radente

Fig..20 Santa Irene luce radente; a) Figura intera; b) Dettaglio volto;

Fig. .20 Santa Irene luce radente; c) Dettaglio parte inf.; d) dettaglio mani.

Fig. .21 San Charalampo; a) Fig. Intera; b) dettaglio volto

Fig. 22. a) San Giorgio; b) San Demetrio

The Icon B grazing light is bad condition, figures on the central panel (Figure 23) reveal gaps of Paint, paint layer, but also the detachment of preparation. The absence of gold on the halos of the two figures is greatly accentuated by the fall of the preparation. On the mantle of the Virgin significant injury of the wooden support at the center of the panel there is a crack that runs along the table.

Fig.23 Figure pannello centrale

On top of the side doors (Fig. 24) are evident falls on the background color and on the figures major gaps on the halos show the wooden support under neath. All this can also be seen on figures of the saints of the lower side of the leaves (Fig. 25)

Fig. 24 Figure parte superiore ante laterali

Fig. 25 Figure parte inferiore ante laterali

3.7 Sampling and Survey in Optical Microscopy

To make a few comments on the paint layers of icon A, restored and on the Icon B, not restored, we were made small samples at the points shown in Fig. 5.1. The samples were taken with the Icon illuminated by wood light in order to identify areas that are not repainted.

Fig.4.5.1 Punti di prelievo nell'Icona A (sinistra) e nell'Icona B (destra)

The samples were observed with an optical microscope in crossed polarizers (from Fig. 5.2 to 5.9, ranked by color of the paint layer) and subsequently analyzed by SEM-EDS in order to identify the constituent elements. On samples taken by the Icon A, is clearly visible a layer of paint recently (Figure 5.5 and 5.6), that for a correct EDS analysis, it was necessary to remove by treatment with solvents, in particular a series of washings with acetone. In all the samples was found the presence of a layer of dirt formed from the dust and other external agents deposited on the layer of paint. The acetone, dissolving partially outside the paint, brought to light the original color, more clear. Similar treatment was done on samples taken by the Icon B.Investing in gold there are only a few areas, because the halos being restored were replenished in purple. The gold standard is presented with microscopic gold-colored metallic-looking areas and darker areas opaque. In the case of the Icon B was not possible to take any sample of Gold because it is completely lost.

The fragments of blue are visibly different observed by light microscopy (Fig.5.9) For the other samples instead are not found significant differences in color between the two icons.

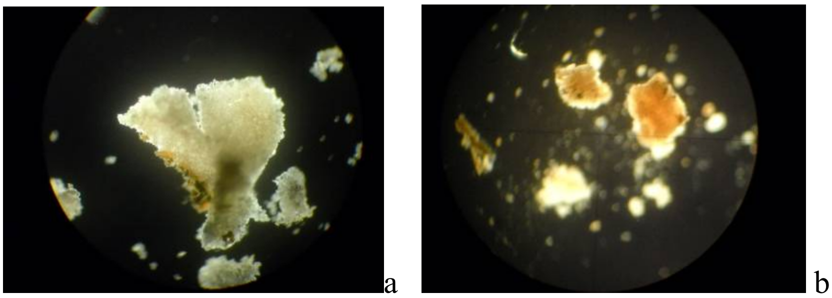


Fig.5.2 Preparazione: a) Preparazione Icona A; b) Preparazione Icona B

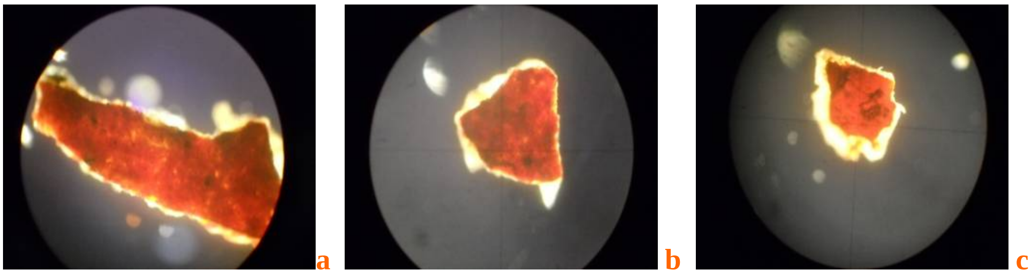


Fig. 5.3 Arancio: a) Frammento dell’arancio prelevato dall’Icona A.

b) Parte dello stesso frammento lavato con acetone.

c) Arancio prelevato dall’Icona B e lavato con acetone.

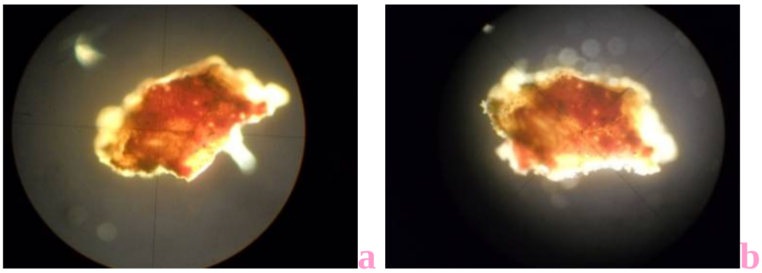


Fig.5.4 Rosa fondo: a) Rosa fondo Icona A, b) Rosa fondo Icona B

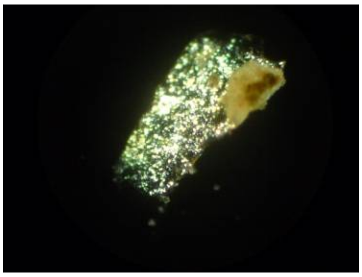


Fig.5.5 Rosa carne Icona A con un’ evidente frammento di vernice esterna trasparente

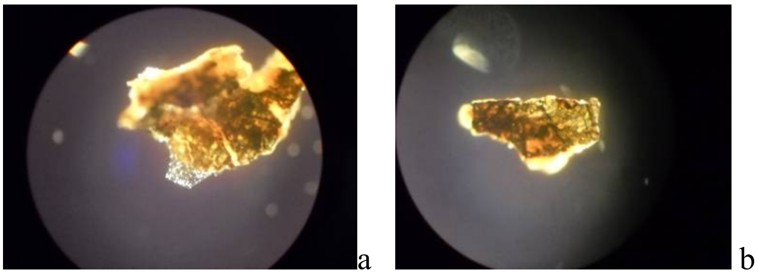


Fig. 5.6 Oro: a) Frammento di oro Icona A, b) Frammento di oro Icona A lavato con acetone

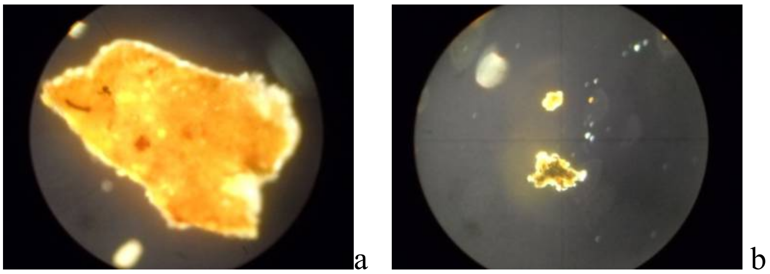


Fig.5.7 Giallo: a) Frammento giallo Icona A, b) frammento giallo Icona B

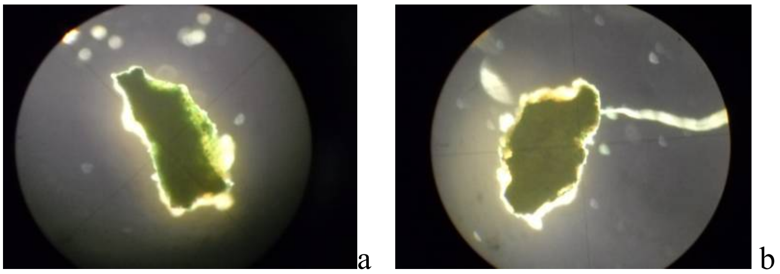


Fig. 5.8 Verde: a) Frammento verde Icona A, b) Frammento verde Icona A lavato con acetone

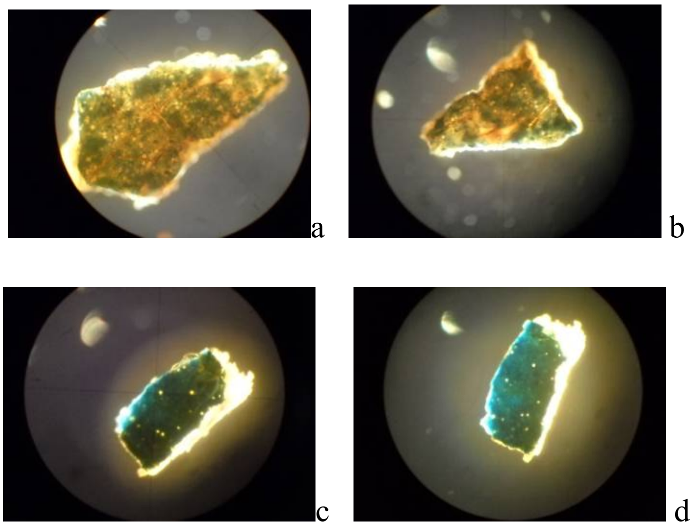


Fig..5.9 Azzurro: a) Frammento azzurro Icona A, b) Frammento azzurro Icona A lavato con acetone, c) Frammento azzurro Icona B, d) Frammento azzurro Icona B lavato con acetone.

3.8 Survey microscope SEM-EDS

The samples were analyzed either to the original state and after washing with acetone, and in the latter case were obtained SEM images and EDS spectra "cleaner".

EDS analysis of the samples, in all cases, the pigments orange, flesh pink and pink background, are constituted by the same elements, namely, C, O, Pb (Spettro.2 and Spettro.3) differing from each other only in the relationship, which is not comparable quantitatively because it may depend on a different amount of the remaining paint. Combining these results with the observation by light microscopy (Fig. 5.3 - Fig.5.4) it can be concluded that the colors were prepared by mixing red lead and white lead In the sample gold, there are both gold and Silver Gold in large quantities, as well as alumino-silicates containing iron (Spettro.4), which suggests that the gilding have been made with silver mecca, silver leaf that is was superimposed on a layer of gold powder and glue. The yellow, in both icons, contain chromium, in addition to lead, carbon and oxygen with impurities of alumino-silicates, and there is therefore presumably a chrome yellow (Spettro.5) The green color shows the apparent discrepancies between the two icons in the Icon A, renovated, shows a different spectrum EDS, Lead-free and that contains Chromium, Cadmium, Zinc, Titanium. Instead in icon B there are zones that have lead and chromium, and areas with aluminosilicates (Spettro.6). Observing the sample of green Icon A carefully in section, however, it is observed the presence of two layers: one, more often, rich in lead, the other, more external, poor oflead (Fig. .4.10), It identifies the pigment rich in titanium and chromium as the next layer, probably added during the restoration.

The blue, observed under the electron microscope (2000 magnification) is composed of a matrix of fine granulometry, as for other pigments, which are incorporated in larger fragments of irregular shape. Icon to the fragments are larger than the icon B (Fig..4.12-4.13).

EDS analysis in the Icon B, over which lead carbon and oxygen, are present Aluminum, Iron and Cobalt; in the Icon A are sodium, aluminum and silicon in significant quantities while there was found the presence of cobalt. These data, combined with the observations in optical and electron microscopy to identify the cause pigment present in the icon in blue as overseas and the pigment present in the B icon as smalt. In this case it was not possible to determine whether the overseas have been added since restoration.

3.9 PREPARAZIONE

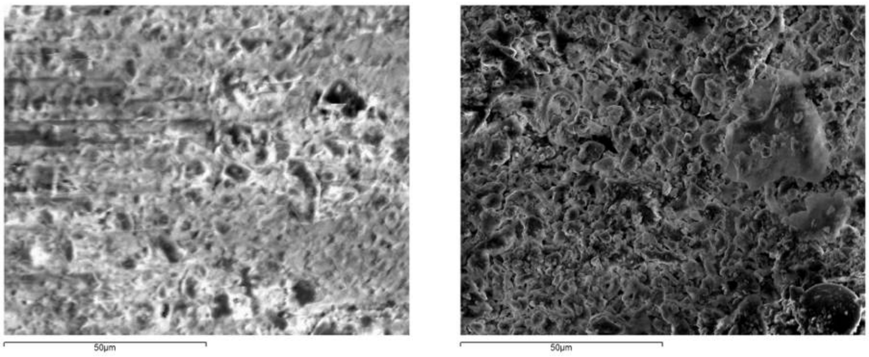
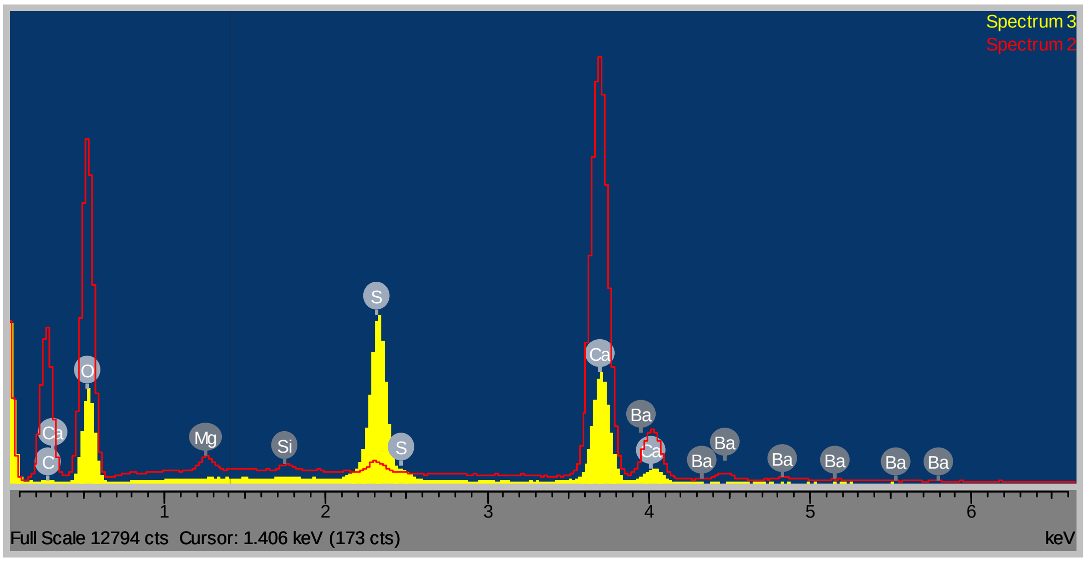


Fig.1 Immagini SEM a 1000X icona A (sinistra) e Icona B (destra)



Spettro.1 - Confronto spettri EDS Preparazione: Icona A = spettro rosso;

Icona B = spettro giallo

Preparazione	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Fe**	**Ba**	**Tot**
Icona A (Spettro 2)	20.49	52.93						0.96			24.23		1.19	100.00
Icona B (Spettro 3)	34.44	51.63	0.32	0.45	2.74	6.03	0.31	0.19	0.08	0.64	2.61	0.56		100.00

Tabella 1. Preparazione (Percentuale degli elementi)

ROSA FONDO E ROSA CARNE

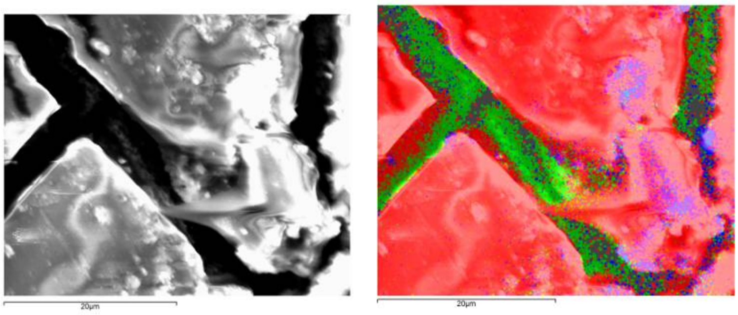


Fig.2 Immagini SEM e mappa EDS a 2000x: Rosa carne con vernice, Icona A Nella mappa EDS, a destra, il rosso indica carbonio, il verde Pb, il blu indica Calcio.

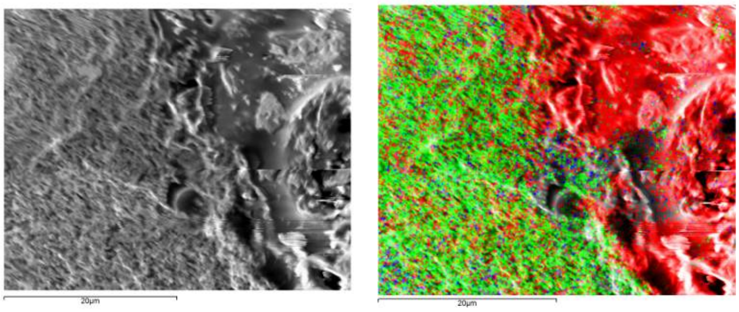


Fig. 3 Immagini SEM e mappa EDS a 2000x: rosa fondo Icona A. Nella mappa EDS, a destra, il rosso indica carbonio, il verde Pb, il blu indica Calcio. La parte a destra, costituita prevalentemente da carbonio è la vernice finale che sovrasta lo strato pittorico

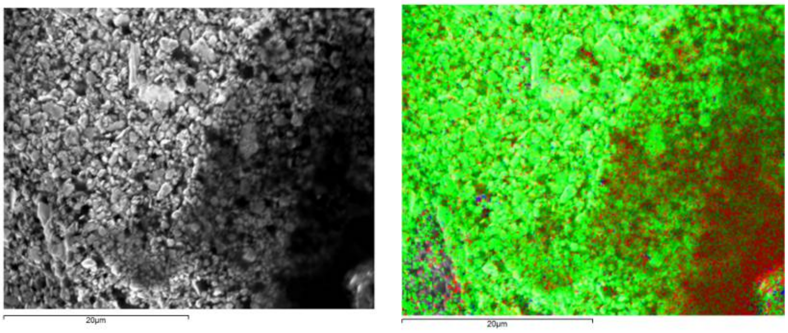
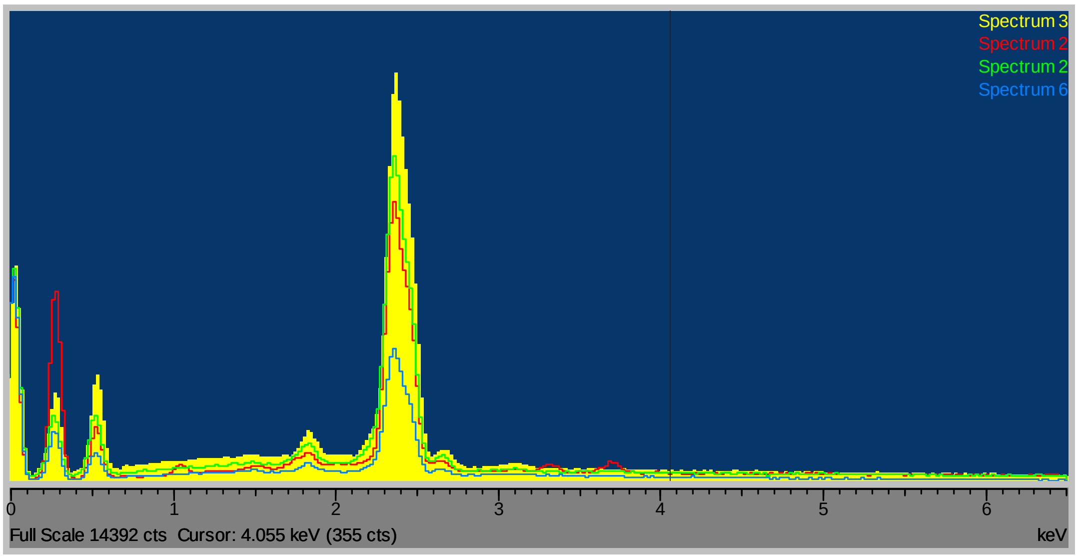


Fig. 4 Immagini SEM e mappa EDS a 2000x: Rosa carne icona B. Nella mappa EDS, a destra, il rosso indica carbonio, il verde Pb, il blu indica Calcio.



Spettro.2 - Confronto spettri EDS Rosa: giallo = rosa carne Icona B; rosso = rosa carne Icona A; verde = rosa fondo icona B; blu = rosa fondo Icona A

Rosa Carne	**C**	**O**	**Na**	**K**	**Ca**	**Pb**	**Tot**
Icona A (Spettro Rosso)	78.29	15.47	0.56	0.46	0.60	4.50	100.00
Icona B (Spettro Giallo)	48.28	41.15				10.58	100.00

Rosa Fondo	**C**	**O**	**Cl**	**Pb**	**Tot**
Icona A (spettro Blu)	65.20	26.64	0.60	7.56	100.00
Icona B (Spettro Verde)	51.71	36.66		11.63	100.00

Tabella 2-3. Rosa Carne – Rosa Fondo (Percentuale degli elementi)

ARANCIO

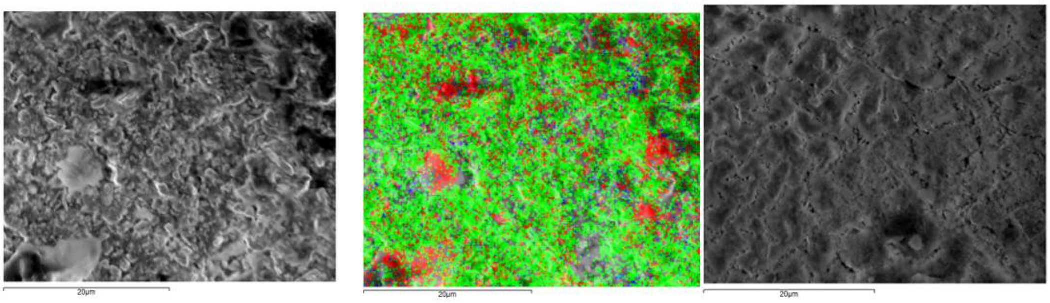
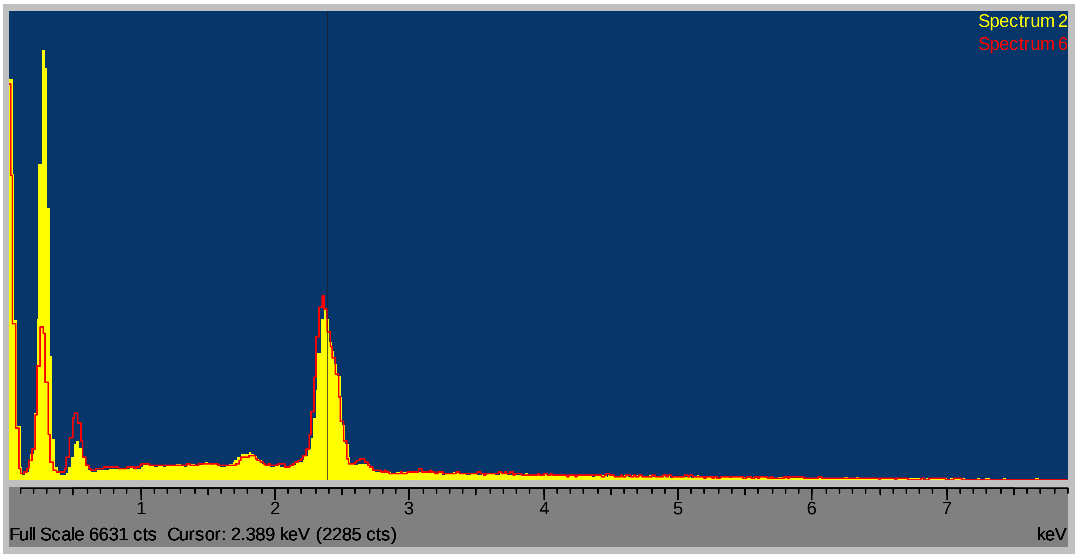


Fig. 5 Immagini SEM e mappa EDS a 2000x: Arancio Icona A (prime due immagini) Nella mappa EDS il rosso indica carbonio, il verde Pb, il blu indica Calcio. Arancio Icona B (ultima Immagine)



Spettro.3 - Confronto spettri EDS Arancio: Icona A = spettro rosso; Icona B = spettro giallo

Arancio	**C**	**O**	**Si**	**Cl**	**Pb**	**Tot**
Icona A (Spettro Rosso)	70.24	24.64	0.28	0.57	4.26	100.00
Icona B (Spettro Giallo)	88.15	9.34			2.29	100.00

Tabella 4. Arancio (Percentuale degli elementi)

ORO

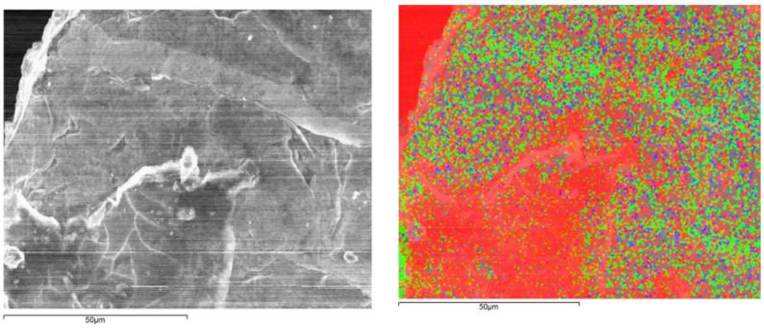
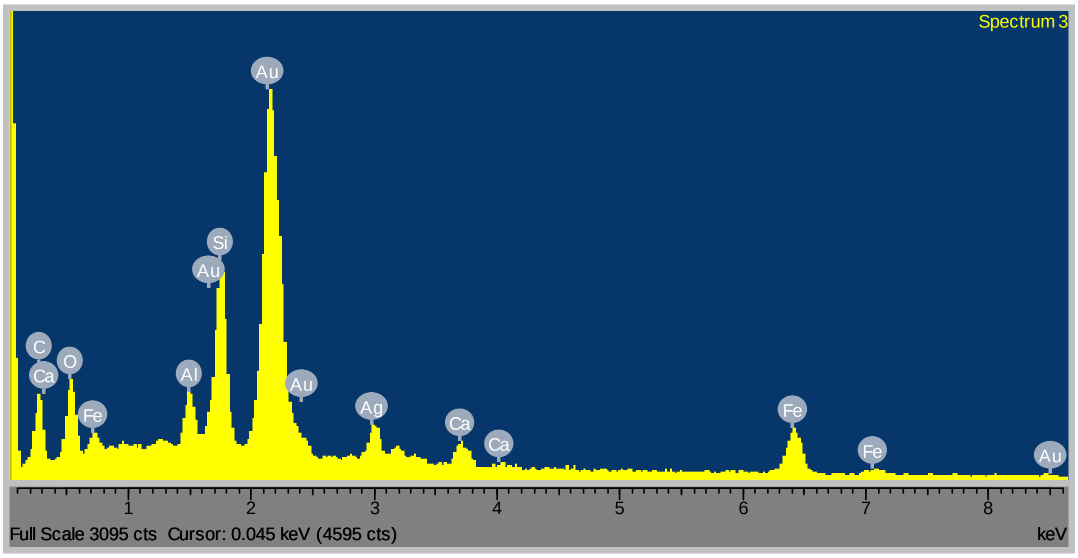


Fig. 6 Immagine SEM e mappa EDS a 1000x del campione Oro dell’Icona A
Carbonio: rosso; Argento: verde; Oro: blu



Spettro.4 - Spettro EDS campione Oro Icona A

Oro	**C**	**O**	**Al**	**Si**	**Ca**	**Fe**	**Ag**	**Au**	**Tot**
Icona A	40.79	28.80	2.62	8.33	1.81	7.21	2.17	8.27	100.00

Tabella 5. Oro (Percentuale degli elementi)

GIALLO

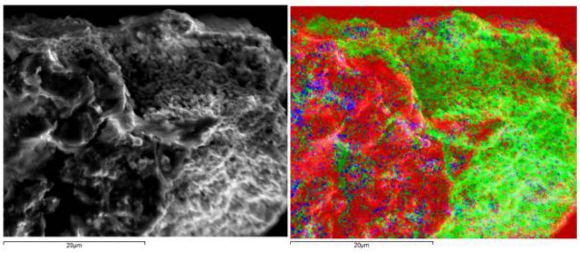


Fig. 7 Immagini SEM e mappa EDS a 2000x: Giallo icona A

Carbonio: rosso; Piombo: verde; Calcio: blu

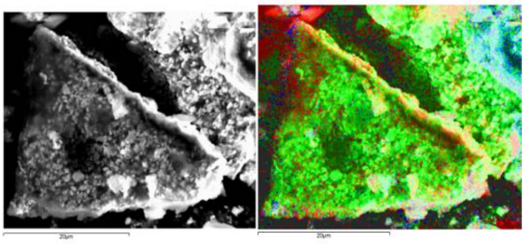
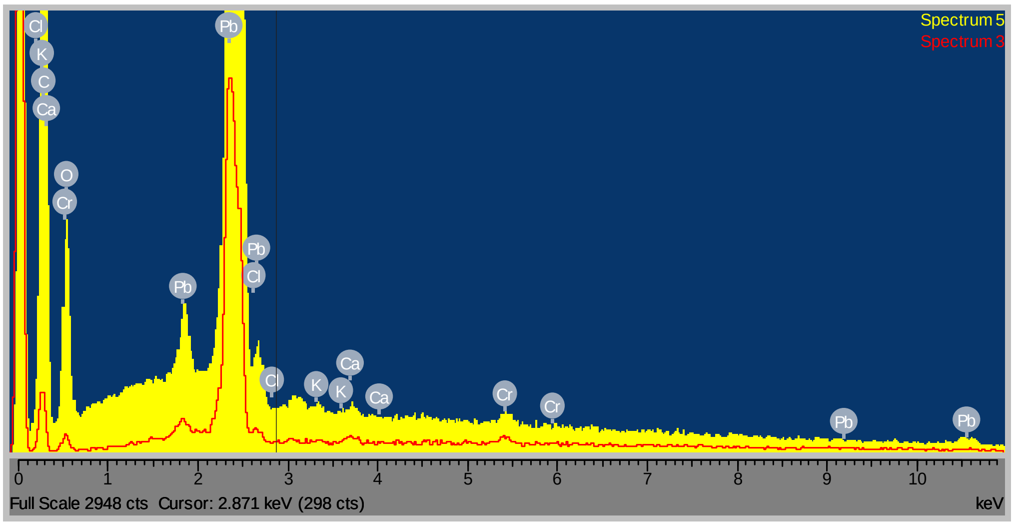


Fig. 8 Immagini SEM e mappa EDS a 2000x: Giallo icona B

Carbonio: rosso; Piombo: verde; Calcio: blu



Spettro.5 - Confronto spettri EDS Gialli: Icona A = spettro rosso;

Icona B = spettro giallo

Giallo	**C**	**O**	**Ca**	**Cr**	**Pb**	**Cl**	**K**	**As**	**Tot**
Icona A (Spettro Rosso)	70.01	10.38	1.25	1.70	16.65				100.00
Icona B (Spettro Giallo)	60.81	16.56	1.39	2.97	15.81	1.12	1.30	0.04	100.00

Tabella 6. Giallo (Percentuale degli elementi)

VERDE

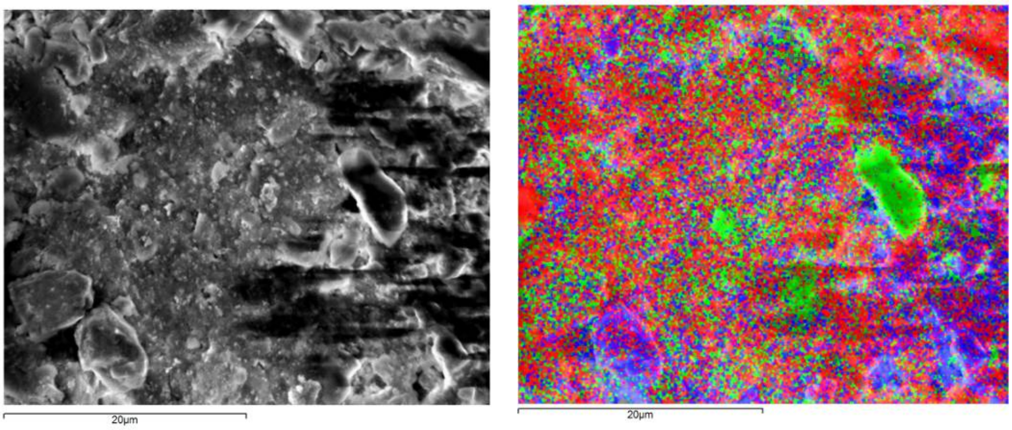


Fig. 9 Immagini SEM e mappa EDS a 2000x: Verde Icona A

Carbonio: rosso; Silicio: verde; Calcio: blu

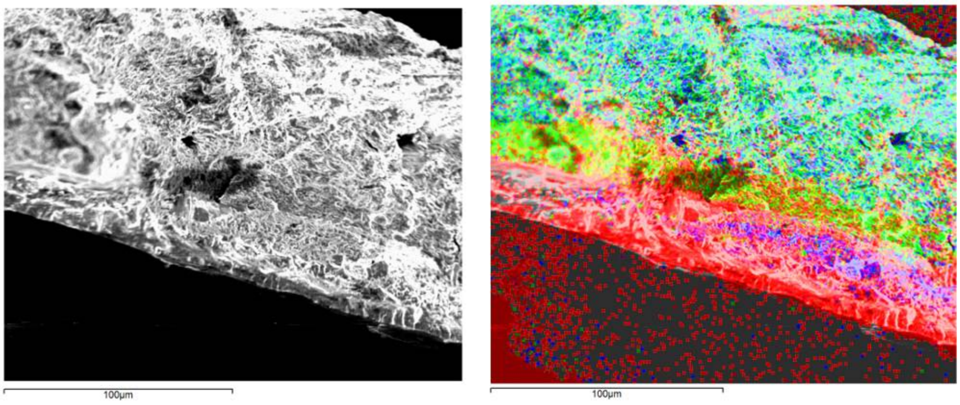


Fig. 10 Immagine SEM a 500x verde Icona A in sezione

Carbonio: rosso; Silicio: verde; Calcio: blu

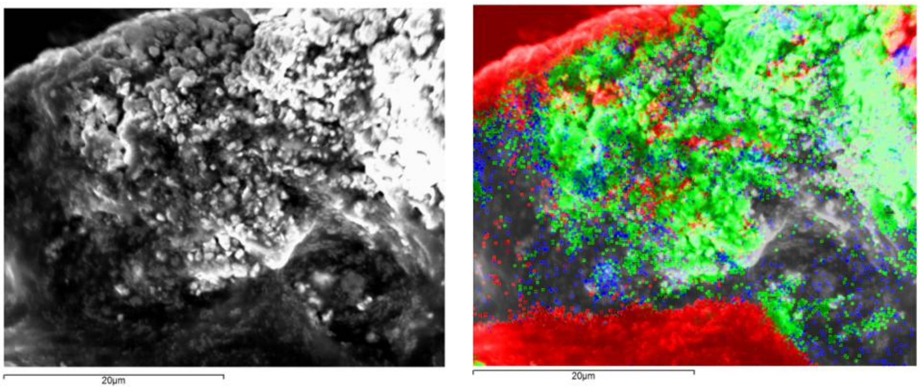
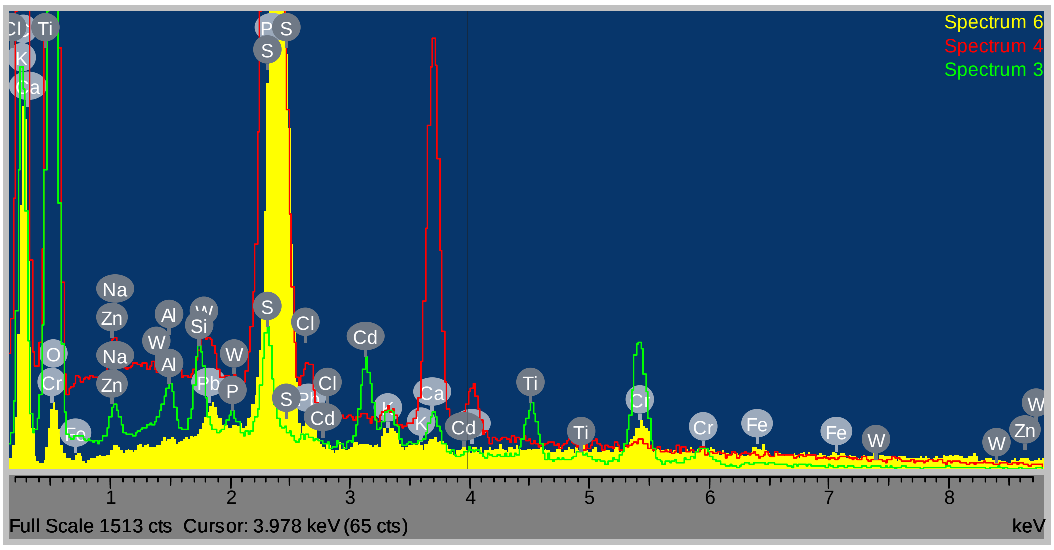


Fig. 11 Immagini SEM e mappa EDS a 2000x: Verde Icona B

Carbonio: rosso; Silicio: verde; Calcio: blu



Spettro.6 - Confronto spettri EDS Verdi:

Icona A = spettro verde (strato pittorico esterno) e spettro rosso (strato pittorico interno),

Icona B = spettro giallo

Verde	**C**	**O**	**Na**	**Al**	**Si**	**P**	**S**	**Ca**	**Ti**	**Cr**	**Cd**	**Fe**	**Cl**	**Zn**	**K**	**Pb**	**Tot**
Icona A Strat pitt estern (SpVerde)	34.19	55.26	0.72	0.49	1.09	0.30	1.32	0.61	1.18	3.73	1.11						100.0
Icona A Strat pitt int (Sp Rosso)	55.73	38.00	0.13	0.04			2.61	2.08		0.07			0.17	0.10	0.09	0.94	100.0
Icona B (Spettro Giallo)	81.00	9.55						0.39		1.60		0.75			0.73	6.21	100.0

Tabella 7. Verde (Percentuale degli elementi)

AZZURRO

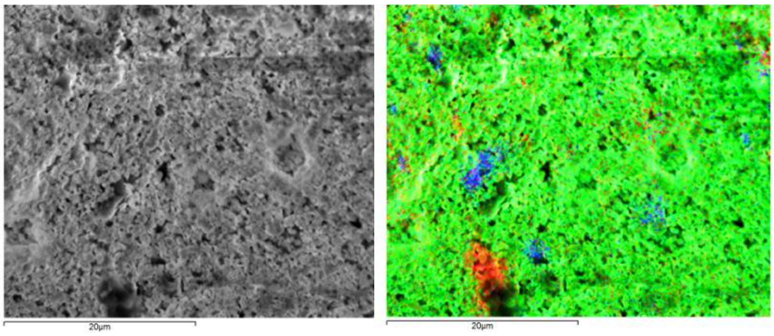


Fig. 12 Immagini SEM a 2000x di un frammento di Azzurro dell'Icona A, dopo lavaggio con acetone. Nella mappa EDS, a destra, il rosso indica carbonio, il verde Pb, il blu indica Silicio.

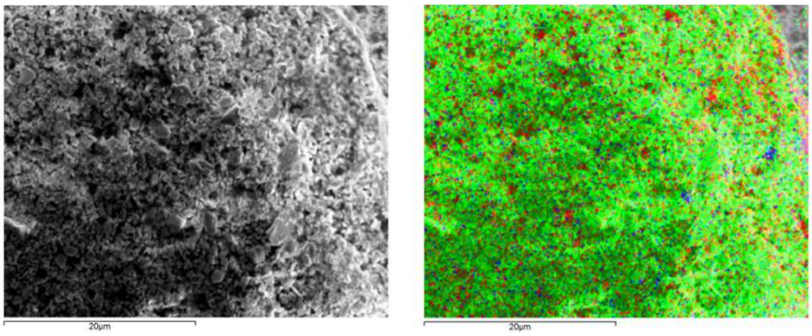
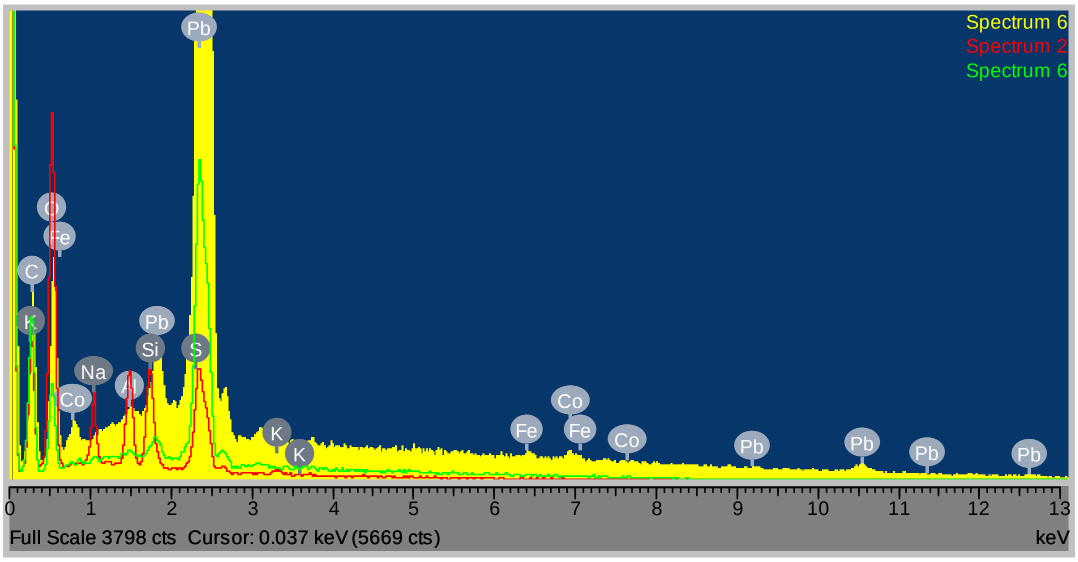


Fig. 13 a) Immagine SEM a 2000x di un frammento di Azzurro dell'Icona B, dopo lavaggio con acetone. b) Nella mappa EDS, a destra, il rosso indica carbonio, il verde Pb, il blu indica Silicio.



Spettro.7 - Confronto spettri EDS Azzurri:

Icona A = spettro verde (zone a granulometria fine) e spettro rosso (frammenti contenenti silicio),

Icona B = spettro giallo

Azzurro	**C**	**O**	**Na**	**Al**	**Si**	**S**	**K**	**Cl**	**Co**	**Pb**	**Tot**
Icona A Zone a granulometria fine (Spettro Verde)	63.66	30.04								6.30	100.00
Icona A Frammenti contenenti silicio (Spettro Rosso)	37,55	51.75	3.23	2.73	2.89	0.44	0.16			1.25	100.00
Icona B (Spettro Giallo)	47.97	40.74						0.67	0.52	9.75	100.00

Tabella 8. Azzurro (Percentuale degli elementi)

Campione	Icona	Elementi presenti	Composto individuabile	Pigmento
Preparazione	A	C, O, Ca; S, Ba, Si, Al, Mg (Co)	$CaCO_3$ con impurezze di Ba e S	Carbonato di calcio
	B	O, S, Ca; C	$CaSO_4$	gesso
Rosa incarnato	A	C, O, Pb; Ca	$2PbCO_3{*}Pb(OH)_2 + Pb_3O_4$	Biacca di Piombo + Minio
	B	C, O, Pb	$2PbCO_3{*}Pb(OH)_2 + Pb_3O_4$	Biacca di Piombo + Minio
Rosa del fondo	A	C, O, Pb	$2PbCO_3{*}Pb(OH)_2 + Pb_3O_4$	Biacca di Piombo + Minio
	B	C, O, Pb	$2PbCO_3{*}Pb(OH)_2 + Pb_3O_4$	Biacca di Piombo + Minio
Arancione	A	C, O, Pb	$2PbCO_3{*}Pb(OH)_2 + Pb_3O_4$	Biacca di Piombo + Minio
	B	C, O, Pb	$2PbCO_3{*}Pb(OH)_2 + Pb_3O_4$	Biacca di Piombo + Minio
Giallo Oro	A	Au, Ag; Al, Si, Fe..		Argento Meccato
	B	-	-	-
Giallo	A	Cr, Pb, C,O ; Al, Si ..	$PbCrO_4$	Giallo di Cromo
	B	Cr, Pb, C,O ; Al, Si ..	$PbCrO_4$	Giallo di Cromo
Verde	A (strato esterno)	Zn, Cd, Ti, S, Cr, Al, Si, Na, P, Ca, C, O	$(ZnS)\cdot CdS + Cr_2O_3 + TiO_2$ + terre	Giallo di Cadmio + giallo/verde di Cromo probabilmente recente (Ti, Cd) non contiene Piombo
	A (strato interno)	Cr, Pb Cr, Pb, C, O; Al, Si, Fe, K …	$PbCrO_4$ + silicati	Giallo di cromo + blu
	B	Cr, Pb, C, O; Al, Si, Fe, K …	$PbCrO_4$ + silicati	Giallo di cromo + blu
Azzurro	A	Na, Al, Si, K; Pb, C, O, S (Ba)	Silicato di sodio e alluminio	Oltremare
	B	Al,Si,K,Co	Vetro potassico con ossidi di cobalto	Smaltino

Tabella 9. Riepilogo risultati analisi EDS e pigmenti corrispondenti

3.10 Opinion

In conclusion, from the comparison of the pigments of the two icons, discloses no differences such as to exclude the common matrix of origin, even if made by different hands and probably, according to the stylistic considerations already exhibited, made at a distance of decades.

The EDS analysis, in particular of the green pigment, denotes the use of colors "modern" such as cadmium yellow and white of the titanium and the absence of lead white, allows us to hypothesize that the restoration "invasive" (carried out following the partial destruction of the icon caused by fire) occurred in recent times.

4. Methods to characterize and dating frescos: study of decoration of the arches the Sanctuary Santa Maria delle Armi.

Questo studio è stato condotto per valutare le potenzialità di due metodologie spettroscopiche: la FTIR in riflessione e la spettroscopia di Fluorescenza X per quantificare lo stato di conservazione di affreschi antichi: In particolare abbiamo focalizzato la nostra attenzione su un caso particolarmente interessante: gli intradossi degli archi decorati a stucco e dorati del Santuario di Santa Maria delle Armi di Cerchiara. Il lavoro di diagnostica è finalizzato alla progettazione del restauro, tuttora in corso.Le figure mostrano le evidenti ridipinture e rimaneggiamenti.

Fig. 1: *Particolare parte superiore dell'arco alla sinistra dell'altare*

Fig. 2: *Particolare parte inferiore dell'arco alla sinistra dell'altare*

Fig. 3: *Particolare dell'arco trionfale*

La nostra ricerca ha mirato all'utilizzo delle suddette spettroscopie per cercare di definire quanto delle decorazioni sia da attribuirsi ai lavori originali e quanto invece sia da imputare alle opere di restauro e rifacimenti che si sono succeduti nel corso dei secoli.

Le misure sperimentali sono state effetuate in situ mediante uno spettrofotometro XRF (per l'identificazione della matrice inorganica) ed uno spettrometro ALPHA FT-IR (per l'identificazione della matrice organica).

Analisi XRF degli stucchi e delle decorazioni delle volte

Sono state effettuate numerose analisi su punti analoghi della stessa decorazione a basso rilievo di stucco dorato che decorano gli imbotti degli archi della chiesa. Di seguito verranno riportati, per ragioni di semplificazione esplicativa, soltanto i risultati riscontrati su più punti di un'unica decorazione presente sul lato sinistro dell'altare. Questi risultati sono risultati descrittivi e rappresentativi di tutti gli altri ottenuti da più parti di entrambe le volte. Le analisi riportate sono state distinte in due parti: parte decorativa (decorazione fiore centrale, decorazioni fiori laterali e rombo in cui la decorazione del fiore centrale è circoscritta) e sfondo (parte bianca che fa da sfondo alle decorazioni) (vedi fig.4). Inoltre in fig.4 sono stati riportati i punti rappresentativi dove sono state effettuate le indagini puntuali di riferimento.

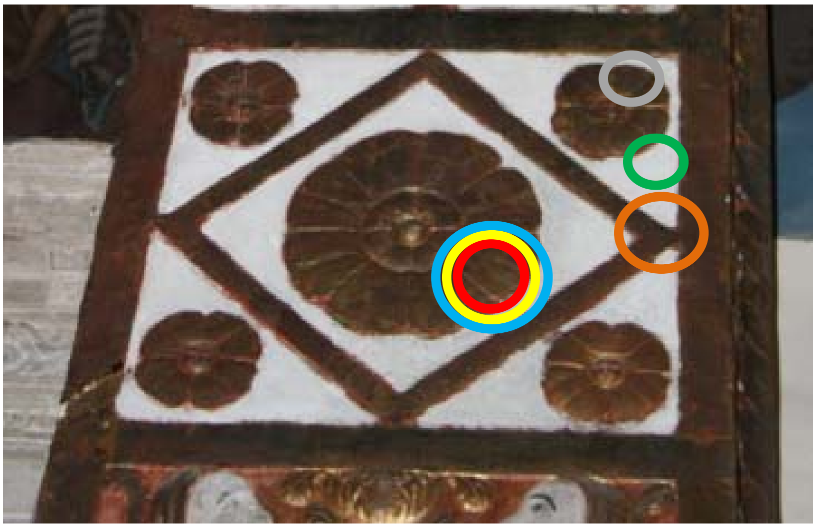


Fig. 4: *Particolare decorazione arco e punti di analisi: rosso(sample1), giallo(sample2), blu (sample3), arancio (sample4), grigio (sample5), verde (sample6)*

Ai rilevamenti diversificati con differenti colori in figura sono stati rinominati come segue:

Nome Campione	***Colore Attribuito***	***Zona di Analisi***
sample 1	Rosso	Parte esterna fiore centrale
sample 2	Giallo	Parte esterna fiore centrale
sample 3	Blu	Parte esterna fiore centrale
sample 4	Arancio	Decorazione rombo
sample 5	Grigio	Fiore angolo destro superiore
sample 6	Verde	Angolo destro sotto fiore

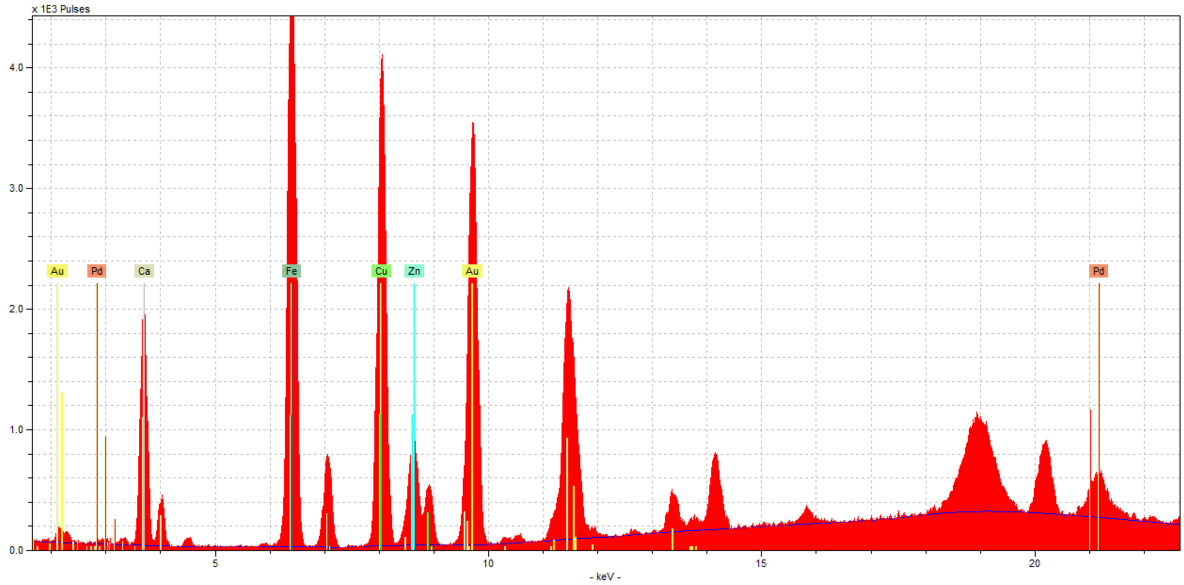
Tabella1: *Descrizione delle zone di analisi e nomi relativi*

Parte decorativa

Per effettuare analisi chimica delle superfici pittoriche,sono stati acquisiti, mediante spettrofotometro XRF, prima gli spettri di una zona della decorazione prima di qualsiasi operazione di pulitura (*sample1).* Successivamente sono state effettuate analisi di zone più profonde della superficie pittorica esposte in conseguenza di operazioni di pulitura (*sample2* and *sample3*). Al fine di stimare l’errore di misura le analisi sono state ripetute in più punti; come esempi di questa verifica, vengono di seguito discussi i risultati ottenuti da due punti di riferimento: uno sulla decorazione a forma di rombo che circoscrive le decorazioni floreali principali (*sample4*) l’altro sulla decorazione del fiore presente nell’angolo destro (*sample5*).

La spettroscopia XRF “vede” solo gli elementi dal terzo periodo in poi della tavola periodica per cui, lasciando non osservati elementi importanti come per esempio, il carbonio (C) o l’ossigeno (O). L’acquisizione del resto degli elementi, congiuntamente all’esperienza chimico-fisica dello sperimentatore in riferimento ai pigmenti e legamti impiegati nella pittura, può fornire la reale composizione delle molecole inorganiche (con inclusione carbonati o ossidi) presenti nelle zone analizzate.

- *sample1*



Spettro1: *XRF del sample1*

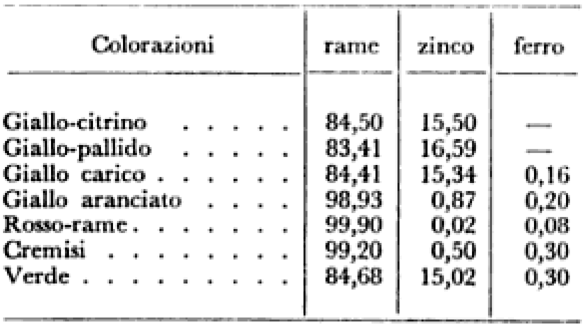
Dallo spettro acquisito, si evince una discreta presenza di Ca, di Fe, di Cu, di Zn e di Au.

- Il segnale del calcio (Ca) è da attribuire al carbonato di calcio ($CaCO_3$). Questo è presente come calcite: il minerale che compone l’intonaco su di cui poggia la decorazione;
- Il ferro è presente come ossido di ferro (con esattezza ossido ferrico: Fe_2O_3), pigmento molto utilizzato negli affreschi e nelle opere murali, in generale per poter dare colorazioni che hanno una variazione di tonalità che può variare dal rosso al giallo a seconda del grado di idratazione che possiede l’ossido del Fe(III);
- Le dorature presenti nella decorazione vengono confermate dalla presenza della riga dell’oro. Infatti. Queste infatti vengono prodotte impiegando un sottilissimo foglio d'oro, di

solito da 22 carati. La foglia d’oro viene applicata su un’adatta preparazione a base di gesso/colla applicata sul supporto, è seguita da una seconda preparazione a bolo macinato in una soluzione di colla.

La presenza del calcio (Ca),oltre che dalle stuccature a gesso è anche attribuibile alla preparazione della doratura. Il gesso, utilizzato per questo tipo di tecnica è infatti il solfato di calcio ($CaSO_4$). Il picco che denota l’abbondanza relativa del Ca, è però di molto superiore al picco che denota l’abbondanza relativa dello zolfo. Ciò indica che il picco del calcio non è esclusivamente imputabile alla presenza del solfato (e quindi del gesso).

- Il picco del rame (Cu) è da attribuire alla porporina. In genere le bronzine o porporine, sono leghe a base di ottone ridotte in polvere e colorate mediante metallocromia . A seconda della gradazione cromatica, la loro composizione può variare sensibilmente. Secondo il **“Nuovissimo ricettario chimico, Volume 1” (HOEPLI EDITORE)** le variabili di composizione come ottone, sono le seguenti:



Colorazioni	rame	zinco	ferro
Giallo-citrino	84,50	15,50	—
Giallo-pallido	83,41	16,59	—
Giallo carico	84,41	15,34	0,16
Giallo aranciato	98,93	0,87	0,20
Rosso-rame	99,90	0,02	0,08
Cremisi	99,20	0,50	0,30
Verde	84,68	15,02	0,30

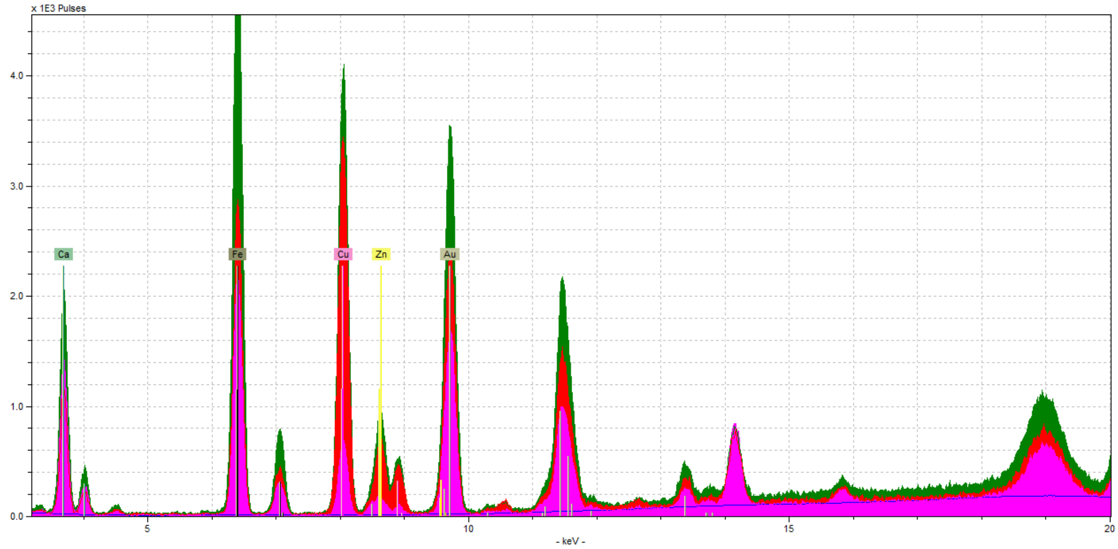
Queste composizioni, giustificano pienamente le ipotesi preposte e le verificano evidenziando una non trascurabile composizione percentuale di zinco rilevato dallo strumento.

Alla luce di questi risultati, è stato possibile accertare che la decorazione originaria fosse del tipo “ a stucco e foglia d’oro 22”. probabilmente applicata con una preventiva applicazione di bolo (argilla). A causa di restauri avvenuti in un secondo tempo, è stata poi applicata la porporina per imitare la foglia d’oro insieme ad una pittura arancione (ossido ferrico), per imitare il bolo. Infatti è prassi comune nel restauro, utilizzare porporina per emulare gli effetti cromatici della foglia d’oro.

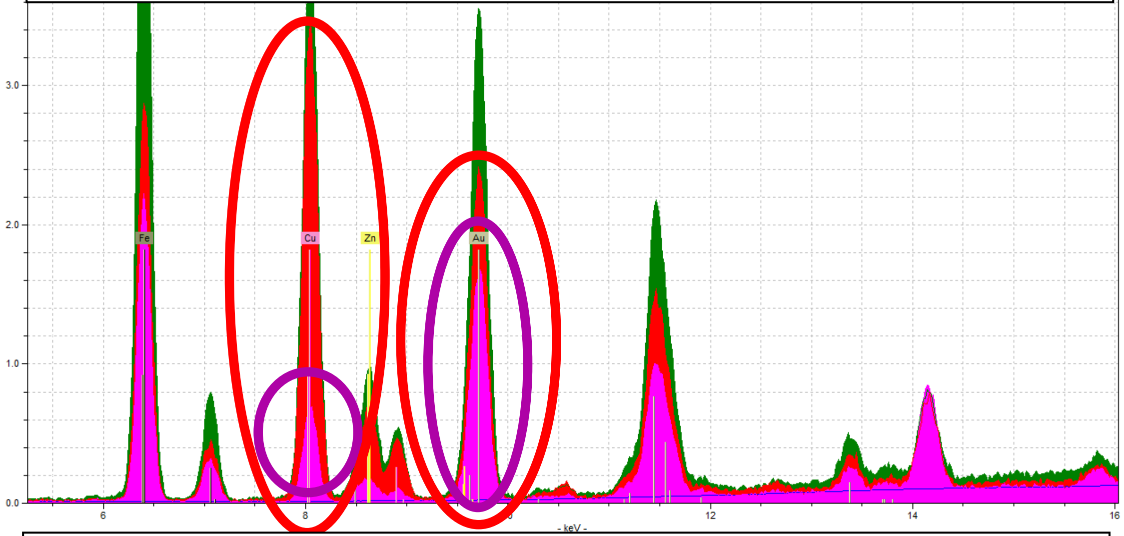
Le suddette conclusioni, sono state confermato delle analisi degli strati più profondità (*sample2* e *sample3*).

- *sample2 e sample3*

Qui di seguito sono stati riportati i dettagli di un *matching* tra gli spettri risultanti da sample1, sample2 e sample3:



matching tra gli spettri risultanti dall'indagine XRF del sample1(in verde), del sample2 (in rosso) e del sample3 (in viola)



dettaglio dei picchi Cα del Fe, del Cu e dell'Au dello spettro risultante dal matching tra il sample1(in verde), il sample2 (in rosso) ed il sample3 (in viola)

Ricordiamo che lo spettro del (*sample1*) è quello della decorazione misurato prima di qualsiasi operazione di pulitura. Mentre il sample 2 (rosso) è quello osservato dopo una leggera operazione.

Dopo una seconda operazione più incisiva è stata effettuata una terza analisi riportata in verde (*sample3*).

Dallo spettro si evince che con l'aumentare della profondità, l'abbondanza relativa del rame e, in minor misura anche del ferro, diminuisce, mentre quella dell'oro tende a rimanere quasi costante.

Lo spettro del sample 3 evidenzia che, una volta tolto il bolo superficiale, l'abbondanza relativa del rame diminuisce drasticamente, mentre quella dell'oro rimane quasi costante.

Questo dimostra la presenza superficiale della porporina (proporzionale all'abbondanza relativa del Cu) e della presenza della foglia d'oro negli strati inferiori.

In tabella 2, vengono schematizzati i risultati diagnostici riguardanti i pigmenti impiegati.

sample	***Zona di campionamento***	***Elementi rilevati***	***Composizione attribuita***	***Pigmento risultante***
1,2,3	Decorazione floreale centrale	Fe	Fe_2O_3	Ocra rossa
1,2,3	Decorazione floreale centrale	Au	Au	Foglia d'oro 22ca.
1,2,3	Decorazione floreale centrale	Fe, Zn, Cu	Lega ottone α ternario (struttura cristallina cubica a facce centrate)	Porporina
1,2,3	Decorazione floreale centrale	Ca	Probabilmente derivante sia da gesso ($CaSO_4*2H_2O$) associato con la preparazione di carbonato di calcio ($CaCO_3$)	*Gesso da Doratori* (chiamato anche *Gypsum*)

Tabella 2: *risultati ottenuti mediante analisi spettrofotometrica XRF*

- *sample4*

L'operazione di rimozione del bolo è stata ripetuta in un altro punto della decorazione (decorazione floreale angolo alto destro) e lo spettro presenta risultati analoghi al precedente.

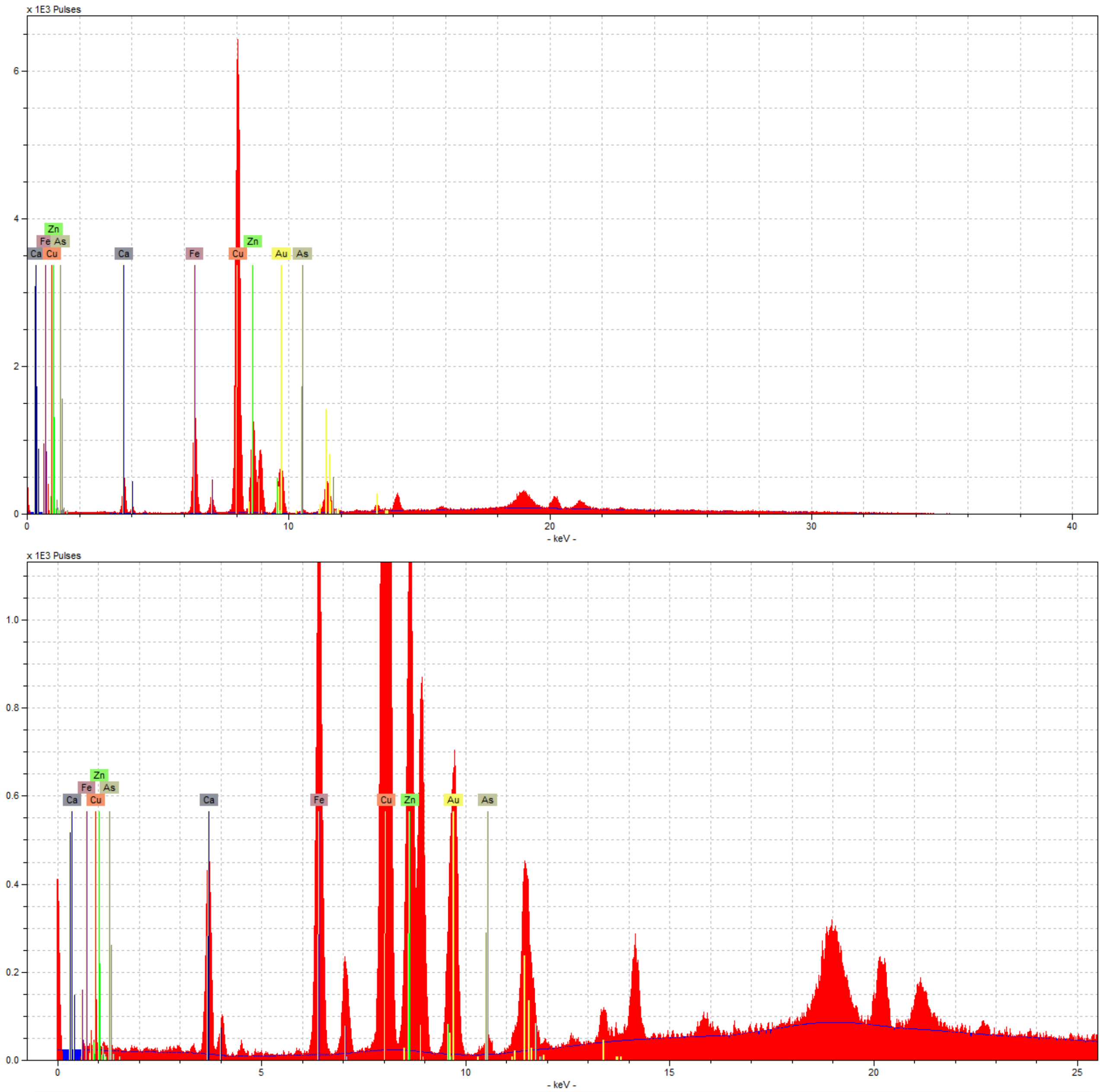
Spettro 4: *risultati ottenuti mediante analisi spettrofotometrica XRF su” sample4”*

sample	***Zona di campionamento***	***Elementi rilevati***	***Composizione attribuita***	***Pigmento risultante***
4	Decorazione floreale angolo alto destro	Fe	Fe_2O_3	Ocra rossa
4	Decorazione floreale angolo alto destro	Au	Au	Foglia d’oro 22ca.
4	Decorazione floreale angolo alto destro	Fe, Zn, Cu	Lega ottone α ternario (struttura cristallina cubica a facce centrate)	Porporina
4	Decorazione floreale angolo alto destro	Ca	Probabilmente derivante sia da gesso ($CaSO_4*2H_2O$) associato con la preparazione di carbonato di calcio ($CaCO_3$)	*Gesso da Doratori* (chiamato anche *Gypsum*)

Tabella 3: *risultati ottenuti mediante analisi spettrofotometrica XRF su “sample4”*

- *sample5*

Un’ulteriore analisi di conferma è stata effettuata sulla decorazione a forma di rombo che circoscrive la decorazione floreale principale.



Spettro5 e spettro6: *risultati ottenuti mediante analisi spettrofotometrica XRF su "sample5" e dettaglio dello spettro*

Lo spettro evidenzia la presenza principalmente del rame, ma con una quantità non trascurabile di ferro, zinco ed oro. I risultati analitici sono riportati nella successiva tabella 4.

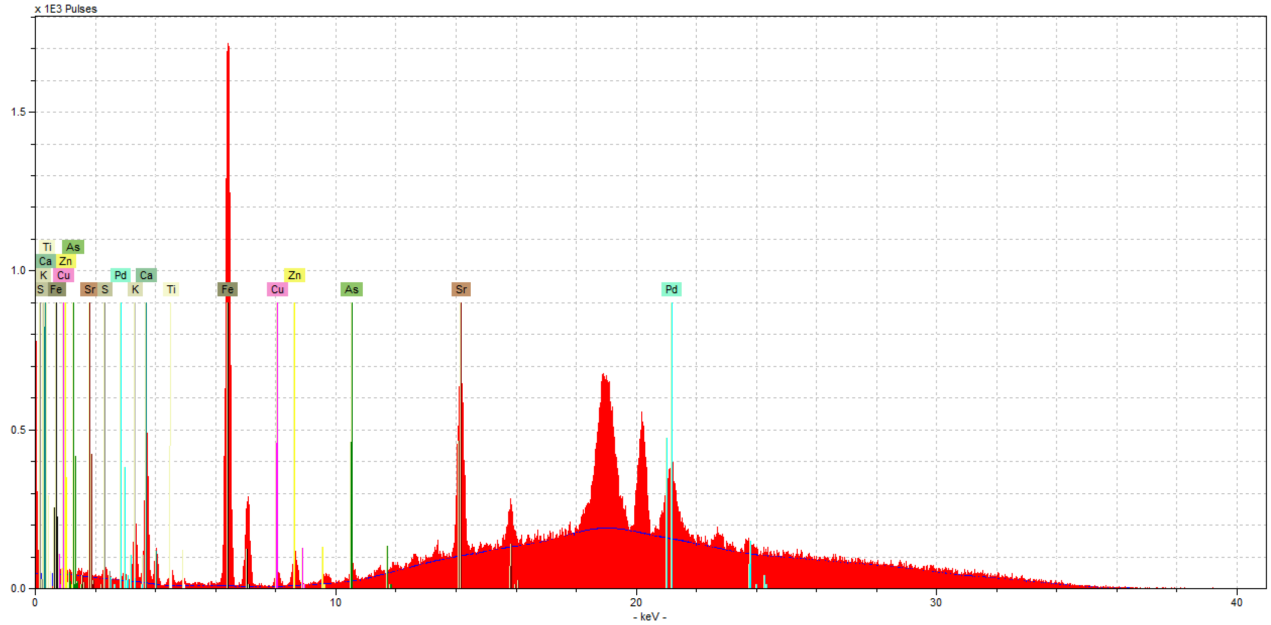
Sample	***Zona di campionamento***	***Elementi rilevati***	***Composizione attribuita***	***Pigmento risultante***
5	Decorazione rombo	Fe	Fe_2O_3	Ocra rossa
5	Decorazione rombo	Au	Au	Foglia d'oro 22ca.
5	Decorazione rombo	Fe, Zn, Cu	Lega ottone α ternario (struttura cristallina cubica a facce centrate)	Porporina
5	Decorazione	Ca	Probabilmente derivante sia	*Gesso da Doratori*

	rombo		da gesso ($CaSO_4*2H_2O$) associato con la preparazione di carbonato di calcio ($CaCO_3$)	(chiamato anche *Gypsum*)

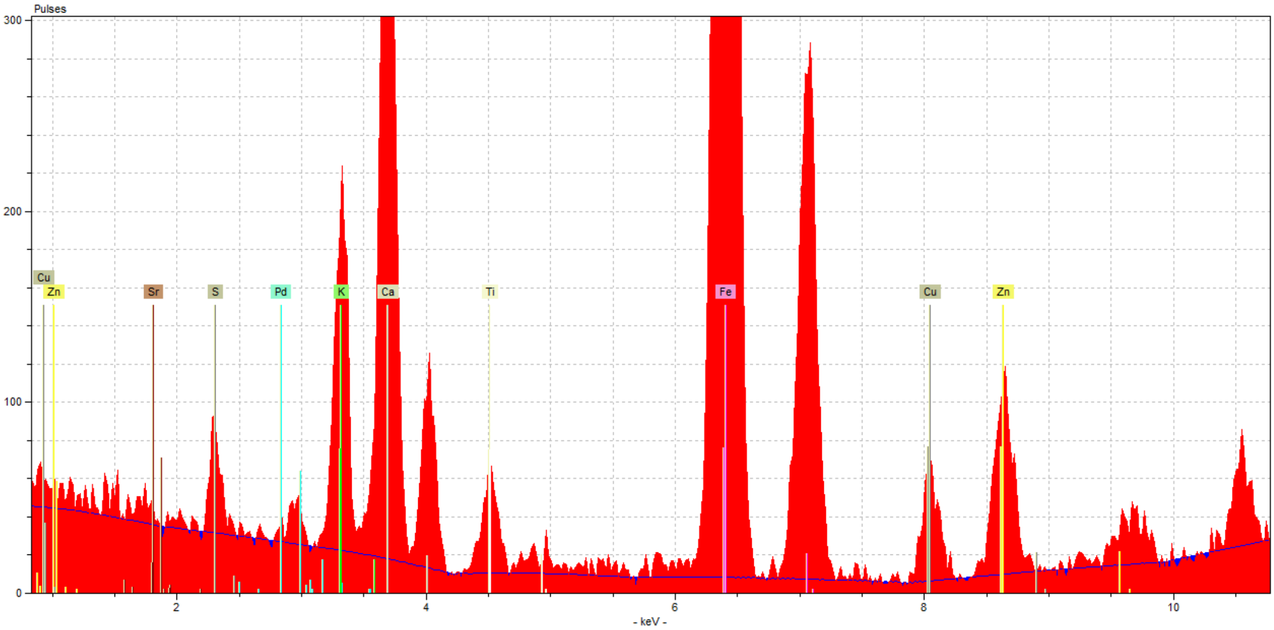
Tabella 4: *risultati ottenuti mediante analisi spettrofotometrica XRF su "sample5"*

Sfondo parte decorativa

Sono state effettuate anche analisi sulla parte tinteggiata di bianco che fa da sfondo alle decorazioni



Spettro7: risultati ottenuti mediante analisi spettrofotometrica XRF su "sample6"



Spettro7: risultati ottenuti mediante analisi spettrofotometrica XRF su "sample6"

Gli spettri evidenziano la presenza principalmente di Ca e di Fe con la presenza di varie impurezze.
Lo zolfo (S) riscontrato nello spettro può far pensare alla presenza di solfato di calcio (gesso) applicato sulla decorazione per donarle aspetto bianco.
Inoltre è stata riscontrata anche una piccola percentuale di titanio (Ti) probabilmente proveniente da un ossido di titanio (esattamente biossido di titanio (IV): TiO_2) utilizzato come pigmento (con il nome di *Bianco di Titanio* o anche *Titanium White*) in commercio solo dal 1920 che per il suo ottimo potere coprente e per essere chimicamente inerte. Storicamente il Bianco di Titanio, viene spesso miscelato con Calcio solfatato o con Bianco di Zinco.
Lo spettro rileva una quantità non trascurabile del picco dello zinco attribuibile proprio all'ossido di zinco (ZnO) che tende a trasformarsi in carbonato di zinco, utilizzato per il buon potere coprente e per la sua resistenza ad agenti atmosferici.
E' la presenza così abbondante del Fe che tende ad insospettire. Difatti il Fe, probabilmente presente come ossido ferrico (ocra), è l'elemento che ha il segnale espresso in abbondanza relativa, più intenso nello spettro. Questo fa pensare ad una ridipintura a base di gesso su di una base color ocra.
La pulitura del gesso (effettuata con acqua) ha confermato questa ipotesi. Sotto la base colorata di bianco, ve ne è un'altra di colore rosso/arancio sicuramente a base di ossido di ferro.
Inoltre, la relativa facilità con cui la tinteggiatura bianca può essere rimossa mediante pulitura con acqua, conferma che si tratta di gesso per doratori, chiamato anche *Gypsum* (solfato di calcio: $CaSO_4*2H_2O$) e non di *bianco San Giovanni* (carbonato di calcio: $CaCO_3$) data la differenza di solubilità in acqua dei due composti. Il solfato di calcio, infatti ha una solubilità in acqua pari a 2gr/l (K_{ps}= $7.10*10^{-5}$) a differenza del carbonato di calcio che ha una solubilità pari a 0.014gr/l (K_{ps}= $4.96*10^{-9}$) entrambi misurati a 298K.
I risultati riportati sono riportati nella tabella 5

Sample	***Zona di campionamento***	***Elementi rilevati***	***Composizione attribuita***	***Pigmento risultante***
6	Sfondo parte decorativa	Zn	ZnO (ossido di zinco)	Bianco di Zinco
6	Sfondo parte decorativa	Ti	Biossido di titanio (TiO_2)	Bianco di Titanio
6	Sfondo parte decorativa	Ca, S	Solfato di calcio ($CaSO_4*2H_2O$)	*Gesso per Doratori* (chiamato anche

				Gypsum)

Tabella 5: risultati ottenuti mediante analisi spettrofotometrica XRF sullo sfondo della parte decorativa

5. Diagnostics Methods to date ancient codices: study the Code Romano Caratelli.

5.1 Scope

These researches did have the aim to study the possibility to use not invasive diagnostic methodologies such as the XRF (X Ray fluorescence) to date ancient codex. In particulr ar the potentialities of this methodology have been tested on the characterization and dating of a manuscript for which has been proposed a dating on the late sixteenth century

5.2 introduction

The work includes 99 watercolors painted on the top half of the page, well made, on watermarked paper of high quality, in excellent condition; on the card are visible some restoration, some stain on the bottom edge and a few flowering. Most of the watercolors have a handwriting artwork in elegant handwriting, indicating also the expenditure for extensions shown, for the restoration and new fortifications. The text also contains a description of the places, distances, types of construction,. The binding, folio. is on parchment, the handwritten titles to the spine, on which there is a gap in shape perfectly square 1cmx1cm.

The work depicts the topographic system of military defense of Calabria Ultra, the relief of the existing fortifications, the design of enhancements and new fortifications. Drawings with mapping function and certainly with dignity strategic military secret. The fortifications are described in detail, primarily towers are strategically had to interface with other towers, to give the alarm in case of attack. All designs are made from land to sea, namely the side that looked better from where he could be a danger. Many experts have suggested a date at the end of the sixteenth century, specifically between 1586 and 1595 and the commitance to the Count of Miranda viceroy under Philip II. The oldest pictorial representations of Calabria known is Saint Pacichelli print of the seventeenth century, the confirmation of this dating brings back a hundred years the knowledge of Calabria through the illustrations.

5.3 Research Activity and Results

10 page sample were subjected to non-invasive diagnostic testing using XRF and FTIR spectroscopy, on each page were made eight points of investigation with XFR and trhee with FT-IR on specific pigment sandinks on paper. The measurements have been performed on the paper in a condition of temperature and relative humidity controlled (23 ° C and 50% RH). The pH, calculated by means of an electrode in contact, reveals an acidity value of 6.1; value which confirms a good state of preservation.

The precise analyzes have been carried out in three steps: in the first place has been carried out the analysis of only one card, and subsequently were "observed pigments of watercolors and ink, in order to separate the spectral content resulting from each these different types of materials.

The analysis on single card, has been carried out in four points (p.1, p. 9, p. 40 and p. 83), the analysis performed by XRF, showed no differences or from a chemical point of view of quality (extracellulosici the components present on the paper were always of the same kind), nor from a quantitative point of view (the relative abundances differ between them a that may fall within experimental error).

The analysis carried out on page 40 (Fig.1), shows the average results compared to the other analysis, for which these values were used (Table 1), to normalize the results obtained from the analysis point of watercolors and inks.

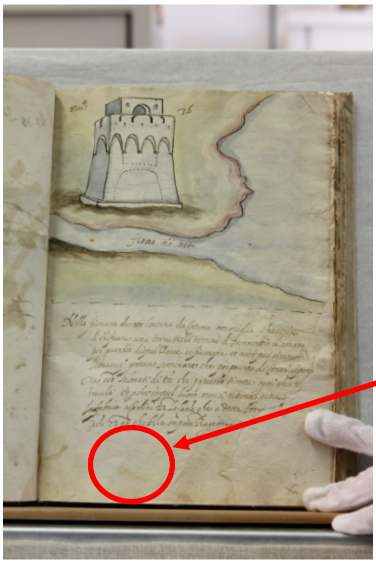


Fig.1: Point on which the instrument is centered on page 40

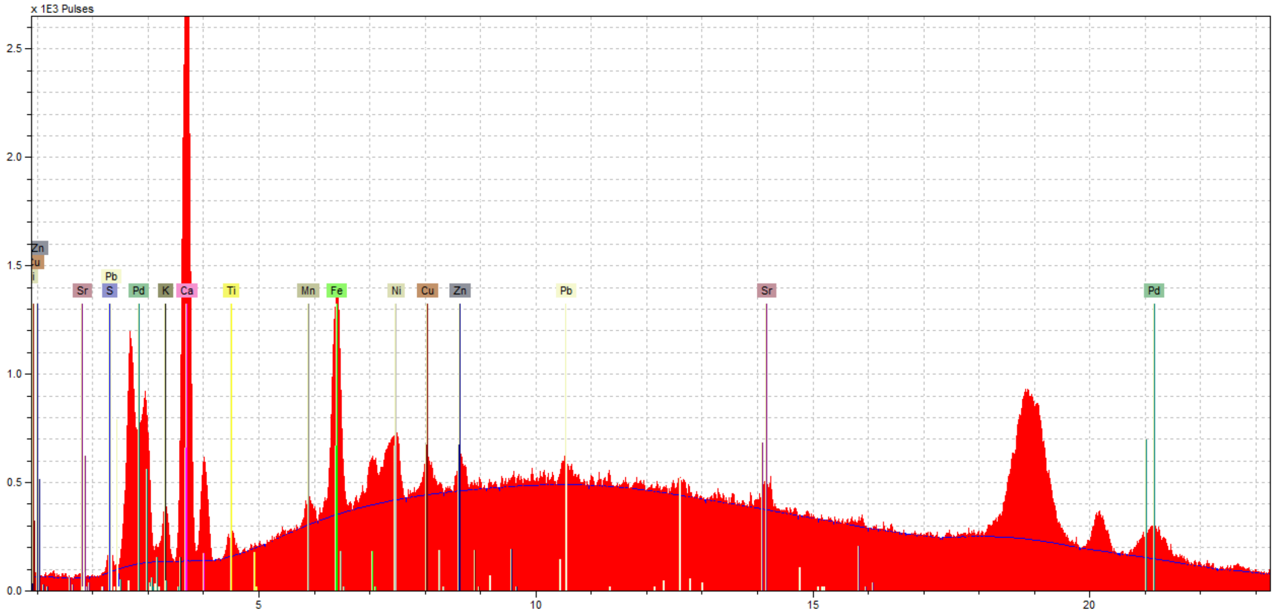


Fig. 2: XRF spectrum (paper pg 40)

Elementi rilevati	***Intensità picco***
Ca	4.0
Fe	1.4
Ni	0.7
Cu	0.6
Zn	0.6
K	0.4
S	0.2
Mn	0.4
Pb	0.6
Sr	0.1
Ti	0.3

able 1: schematic of the results obtained from the spectrum shown in Figure 2 as a function of the data obtained and their relative abundance

The examination of the pigments, the results of whic *XRF2* obtained by subtracting the data obtained from the analysis of the single card (Tab. 1) to those relative to each acquired spectrum, showing in all areas analyzed, a high presence of lead white (ancient pigment used until the end of the eighteenth century) and small amounts of iron oxides (components of the land). Evidently the watercolor paints were all prepared by dissolving small quantities of lands (siena, burnt or natural) in the lead white, while the binder is gum arabic (identified the nature of the impurities encountered in the analysis). Blue is probably an indigo: ancient pigment dissolved in white lead that do not record the signal being of the organic component undetectable all'XRF. In sample function, is shown below the analysis performed for the sample XRF2:

Fig. 3: area of analysis of the sample page 9 XRF2

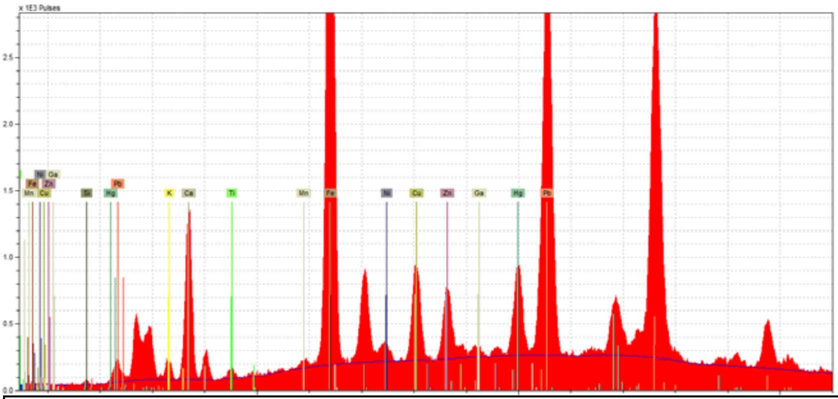


Figure 4: XRF spectrum

menti rilevati	***Intensità picco XRF2***	***Intensità picco (carta)***	***Intensità normalizzata del segnale XRF***	***Composizione risultante***
Pb	3.5	0.6	2.9	$PbCO_3$
Fe	3.9	1.4	2.5	Fe_2O_3
Ca	1.4	4.0	/	/
Cu	0.9	0.6	0.3	$CuCO_3$
Zn	0.8	0.6	0.2	(impurezza)
Hg	0.9	/	0.9	(impurezza)
Ni	0.4	0.7	/	/
Ga	0.3	/	0.3	(impurezza)
K	0.2	0.4	/	/
Mn	0.2	0.4	/	/
Ti	0.2	0.3	/	/

Table 2: schematic of the results obtained from the spectrum presented in Figure 4 as a function of the data obtained and their relative abundance

In Table 2, by XRF spectrum obtained from analysis of the pigments on paper, are subtracted values of table 1 (the single card) for obtaining normalized intensity of marks which are obtained from the compositions of the pigments. In the spectrum analysis, on a base of lead carbonate (white) were used a mixture of iron oxides (brown color) and carbonates of copper (green). The spectrum indicates a non-negligible amount of mercury resulting probably from the lead: it was common fact that the Hg was present as an impurity in the manufacturing process of lead carbonate. This hypothesis is corroborated by the fact that the presence of mercury is always linearly proportional in all the spectra analyzed with the relative abundance of lead. The inks were analyzed in a similar manner.

Fig. 5: the area of analysis of the sample page 83 XRF7

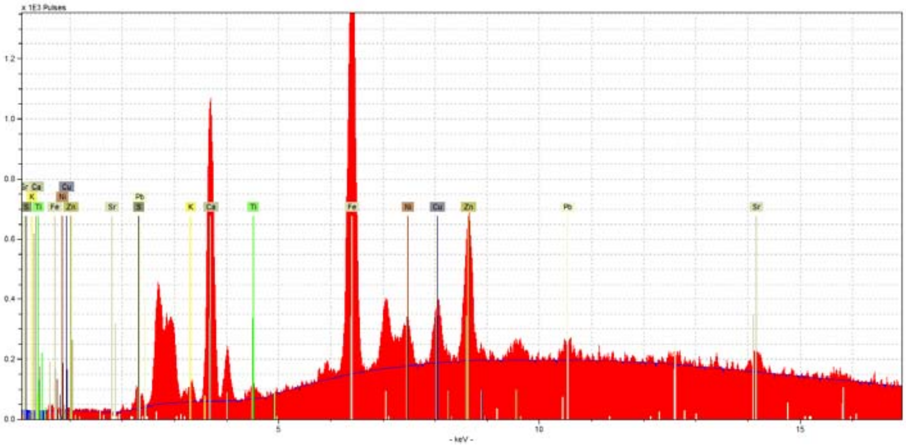


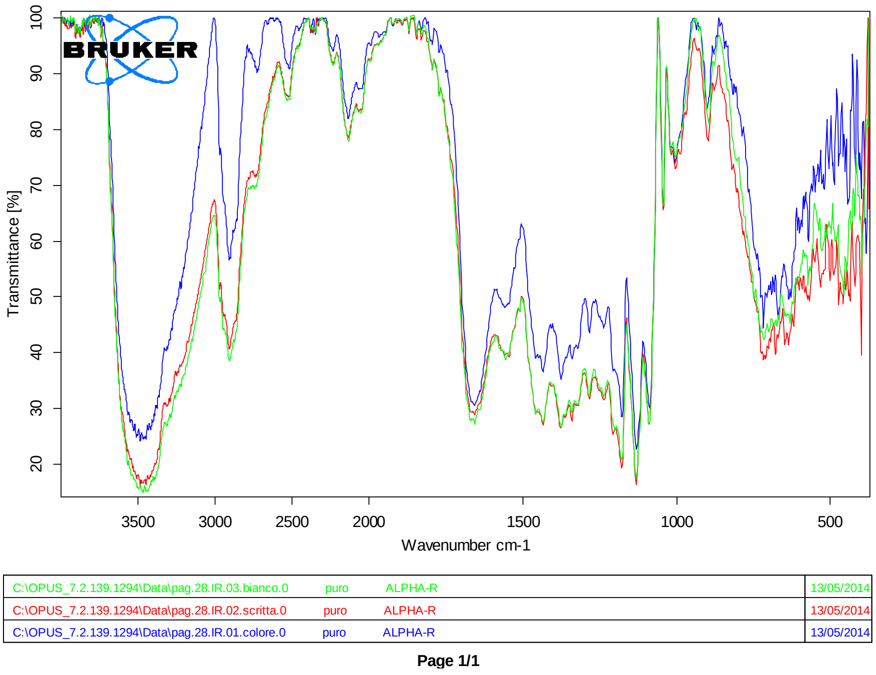
Figure 6: Spectrum obtained following the analysis by XRF spectrometer

Elementi rilevati	***Intensità picco***	***Intensità picco (carta)***	***Intensità normalizzata***	***Composizione risultante***

			del segnale XRF	
Pb	0.2	0.6	/	$PbCO_3$
Fe	2.4	1.4	1.0	Ink iron gall
Ca	1.1	4.0	/	/
Cu	0.4	0.6	/	/
Zn	0.7	0.6	0.1	/
Ni	0.3	0.7	/	/
Ti	0.2	0.3	/	/
K	0.1	0.4	/	/

Table 3: schematic of the results obtained from the spectrum shown in Figure 6 as a function of the data obtained and their relative abundance

The results reveal a discrete presence of iron, it is gallic inks iron, organometallic compounds of the nature of iron chelated with groups of gallicacid.The origin of this ink is ancient, In the Middle Ages the monks manufactured inks; by the many recipes of the fifteenth century, it does indicate that the iron-gall ink was well known and used. In the sixteenth century there is much literature on these inks and their properties, in the seventeenth century English physician and chemist William Lewis shows how the color of the inks did not depend only on the metallic iron, but by a reaction with the extract plant (gall), a statement later confirmed by J. Ribacourt. Since the eighteenth century, prepared as test new compounds based on ammonium vanadate and walnut extract of Gaul fading light and then immediately to the compounds derived from the action of potassium chromate of extract of logwood, until 1856 when Lehonardi patenting its ink alizarin that unlike the older ones that were not substantially more than actual suspension of the dyes and the dyes iron gallic first iron and iron-gallic tannin then in solutions of gum arabic, was a clear liquid that is could filter and in which were contained and not combined tannic and gallic acids, salt, iron, an acid (eg, hydrochloric acid) that prevented the combination and the dye alizarin. The combination of iron sulfate and gallic acid with the formation of the compound iron gall that made the writing black, was done on paper and then in the presence of reagents contained in the air (ammonia).
In the second analysis, for each page three surveys were carried out by IR spectrophotometer for identification of functional groups of organic pigments, bindersorinks. The functional groups of the IR spectra, however, have not led to no useful result, since the functional groups of the cellulose polymer of which the glucoside is mainly composed of the paper, covering all the useful signals of the functional groups of pigments and binders



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C:\OPUS_7.2.139.1294\Data\pag.28.IR.01.colore.0	puro	ALPHA-R	13/05/2014

Page 1/1

Figure 7: matching between the IR spectra of page 28

The spectrum of Figure 7 shows the matching between the three tests carried out on the watercolor on page 28, and on the ink on the paper.

The spectrum shows a band identification of the OH stretching at 3500cm-1; in the region of 1577 cm-1 fall vibrations of different groups, in our case the stretching C = C and C = CO and asymmetric stretching OC = O.

The presence of these functional groups is confirmed by other typical bands. It can also form more adjacent carbonyl groups, which can give rise to keto-enol tautomerism, with formation of groups C = CO.

The matching, although showing the differences between the spectra analyzed (in particular between the part and that of watercolor inks and paper), does not show discriminating which may have analytical valence.

Lo spettro di figura 7, mostra il matching tra i tre test effettuati sulla pag.28 sulla parte dell’acquerello, sull’inchiostro e sulla carta.

Lo spettro indica una banda identificativa dello streching dell’O-H a 3500cm^{-1}; nella regione dei 1577 cm^{-1} cadono le vibrazioni di diversi gruppi, nel nostro caso gli stretching C=C e C=C-O e lo stretching asimmetrico O-C=O.

5.4 Conclusions

The pigments dissolved in gum arabic used for the realization of the paints are: the white lead or lead white pigment which is a pictorial inorganic consisting of basic lead carbonate (II). Known and used since ancient times has been the only white available with the "white St. John" (calcium carbonate) until the nineteenth century; later, with the introduction on the market of zinc white (in about 1840) and, in the twentieth century (about 1930) of titanium white, its use is quite diminished almost to disappear altogether; small amounts of indigo dissolved in white lead to the creation of the blue, a color origineve getale extract from 'gualda grass, grown in areas of Fyvie in Nocera Umbra. The ancient preparation consisted of a first fermentation in water and then adding the lime, and after a short air oxidation, is formed pigment blue. In ancient times it was used together with white lead to get a similar color all'azzurrite; yellow ocher and lands which are pigments of mineral origin used since prehistoric times, composed of hydrous iron oxides, silicates and clays. Their main component is the limonite. Their hue varies depending on their place of origin. The ink is iron-gallic The coloring of the ink is due to its main component, gallate iron, obtained by the reaction of a generic tannin with a ferrous salt. When the reaction is carried out with the components of tannins and metal salt in the ratio of 4: 1 all the iron is complexed by the tannin thus producing a chemically stable ink where the gallate iron behaves as a pigment. In these conditions, however, the reaction takes place with a certain slowness and time is needed because the reaction takes place completely. So if the ink was used immediately after preparation behaved in reality by becoming indelible dye. Furthermore, in those proportions needed a few seconds of exposure to air to achieve complete oxidation (blackening and relative) of the iron in the compound. For this reason it tended to add an excess of metal salt that, if one part made immediate blackening of the ink, the other side made unstable compound into purchasing strong oxidizing properties. It should also be noted that while the ink color is black maintained for periods of several years, later, took the oxidation of all the iron in excess of the compound occurred a change of color to brown more or less dark. There are many recipes in the fifteenth century in the sixteenth century, there is much literature on these inks and their properties, in the seventeenth century English physician and chemist William Lewis shows how the color of the inks did not depend only on the metallic iron, but a reaction with the plant extract (gall), a statement later confirmed by J. Ribacourt. Since the eighteenth century, prepared as test new compounds based on ammonium vanadate and walnut extract of Gaul fading light and then immediately to the compounds derived from the action of potassium chromate of extract of logwood, until 1856 when Lehonardi patenting its ink alizarin that unlike the older ones that were not substantially more than actual suspension of the dyes and the dyes iron gallic first iron and iron-gallic tannin then in solutions of gum arabic, was a clear liquid that is could filter and in which were contained and not combined tannic and gallic acids, salt, iron, an acid (eg, hydrochloric acid) that prevented the combination and the dye alizarin. The combination of iron sulfate and gallic acid with the formation of the compound iron gall that made the writing black, was done on paper and then in the presence of reagents contained in the air (ammonia). The XRF analysis give us spectrum which shows the presence of iron, gallic acid is not readable because of an organic nature, so it would seem an iron gall ink made from an old recipe still not modified byin-depth studies in the seventeenth century.The materials and techniques used support the proposal date, no scientific data can refute it, but no result allows a scientific confirmation of the date at the end of the sixteenth century.

6. Diagnostic methods to study ancient paints: the case of scientifical attribution of works by Gregorio and Mattia Preti (collaboration with Heritage Malta and Opificio delle Pietre Dure di Firenze)

6.1 scope

In this part of the research work several scientific methodologies have been used to verify the possibility to identify the authors of ancient paints. In particular , the works of the two artists: Gregorio and Mattia Preti have been studied by X Ray, SEM-EDX and IR spectroscopy, to attribute correctly paints for which the historical attribution to these authors was still under discussion.

6.2 introduction

Gregorio (1603/1672) and Mattia (1613/1699) Preti ,two brothers artists borned in Taverna of Catanzaro. Gregorio leaves Taverna for Rome in 1628, Mattia in 1633. The study examines a group of works by Mattia and Gregorio Preti, sample works, of which the date and the attribution are certain to obtain objective data to be compared with the rest of their production of still uncertain origin and authenticity.

The seven works are:

- La Madonna della Provvidenza;
- La Madonna della Purità;
- San Martino Vescovo e Santi;
- Ritratto di un monaco domenicano;
- San Pietro e San Paolo;

- La predica di San Giovanni Battista;
- Jaele uccide Sisara.

The first two are works of the two brothers together, the third and fourth are Gregorio's works the last three just Mattia's works main analyzes carried out**:**

Non-invasive analysis

UV light (λ from 10 to 400 nm) useful for investigating the most superficial layer of the work and identify any recent restoration and repainting.

X-rays (λ from 10 to 0.01 nm) are used to obtain information on the painting technique, on any underlying drafts and help establish the authenticity of a work reflectography IR-The infrared (λ> 780 nm) are used to highlight the presence of preparatory drawings and any repentances, since having a greater wavelength of the UV rays can reach the preparatory layer.

Invasive analyzes

Exams stratigraphic sections in the visible and UV optical microscope FT-IR spectrophotometry .

The UV showed, in the painting of Our Lady of Providence, numerous additions of the restoration along the sides, the most visible are localized on the knee of San Francisco and in the central area, where there is an irregular vertical integration from the hand of the angel on the left to the base of the painting.

Fig.1 Mattia e Gregorio Preti, *La Madonna della Provvidenza*

Fig.2 Mattia e Gregorio Preti, *La Madonna della Purità*

In Our Lady of Purity little adjustments and glazes integration occur in a diffuse way. Broader integrations are located in the central area and at the top between the two saints and along the edges. The painting has suffered a lot of damage for the theft of the painting in 1970 with the UV examination of color of the painting of San Martino and Saints appears many additions materials and colors that cover large parts of the canvas, especially on thebottom

Fig.3 Gregorio Preti, *San Martino vescovo e Santi*

With the examination under oblique light, the color has extensive abrasions, craquelure and micro-decoesioni , especially in areas where it is greater use of brown (robe of St. Francis and St. Rocco on the right).

With the examination under oblique ligth has also highlighted the characteristic executive of engraving color, still soft, with the use of a rigid tip for the execution of the decorative details of the dress of San Martino. This technique was also used for the decorations of the dress of San Gennaro in Our Lady of Purity, both Gregorio's works. In Jael killing Sisera, significant responses were obtained by oblique light and x-ray examinations. The painting has always been attributed to Mattia Preti for the great similarity with his documented Allegory of Vanity, shows the presence of the same tracks on the turban of Jael. in this painting was used the same technique of the decoration used as decorative elements in the San Martino and the Lady of purity. technical attributed to Gregorio Preti and that is not in the Vanity of Mattia

Fig.4 Gregorio Preti, *Jaele uccide Sisera*

Fig.5 Mattia Preti, *L’allegoria della Vanità*

The application of infrared reflectography did not reveal the presence of preparatory drawings for the works of collaboration and for those attributed to Gregorio Preti, but instead they are in the works attributed to Mattia.

In particular, the infrared examination showed a preparatory drawing very accurate, also equipped with light and dark in the painting of the preaching of John the Baptist with the self-portrait of the artist.

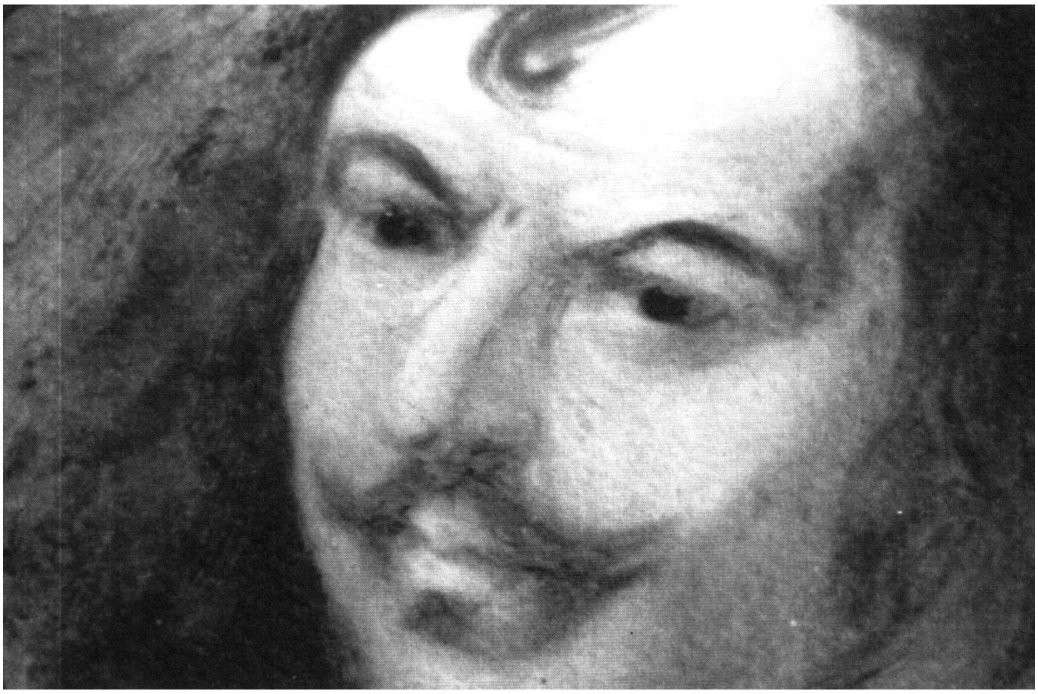

Fig.6. Mattia Preti, *La predica di San Giovanni Battista*; particular of preparatory drawing

The X-ray image of Our Lady of Purity looks very opposed to the large presence of radiopaque material (White Lead). The image of St. Nicholas is reworked from the version below, the miter was enlarged, the cope modified both in form and in the decorative elements and the pastoral is seen in two versions side by side

Fig.7 Mattia Preti, *San Pietro*, x ray image

In Portrait of a Dominican friar, radiograph shows the canvas fixed to the frame through a series of nails. You notice regrets over his left shoulder, the right corner of the book and the fingers of his right hand shots appear more than once. In the light colors it is possible to see the use of short strokes made by successive layers and stacked to achieve the desired volume (typical technique of Gregorio).

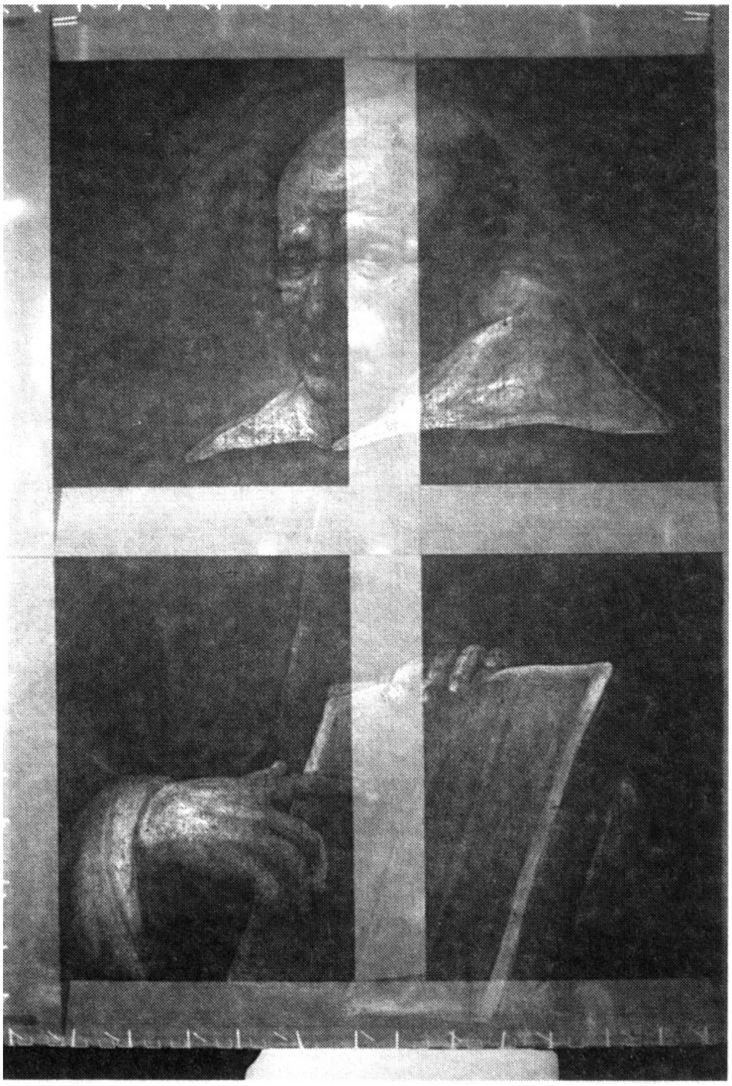

Fig.8 Gregorio Preti, *Ritratto di un domenicano* x ray image

The X-ray image of St. Peter and St. Paul shows the presence of another underlying paint layer performed with radio-opaque material very thick. Inverting the plate is evident a half-length figure,it is possible to see:the halo the miter and the crosier on the left corner of the painting.

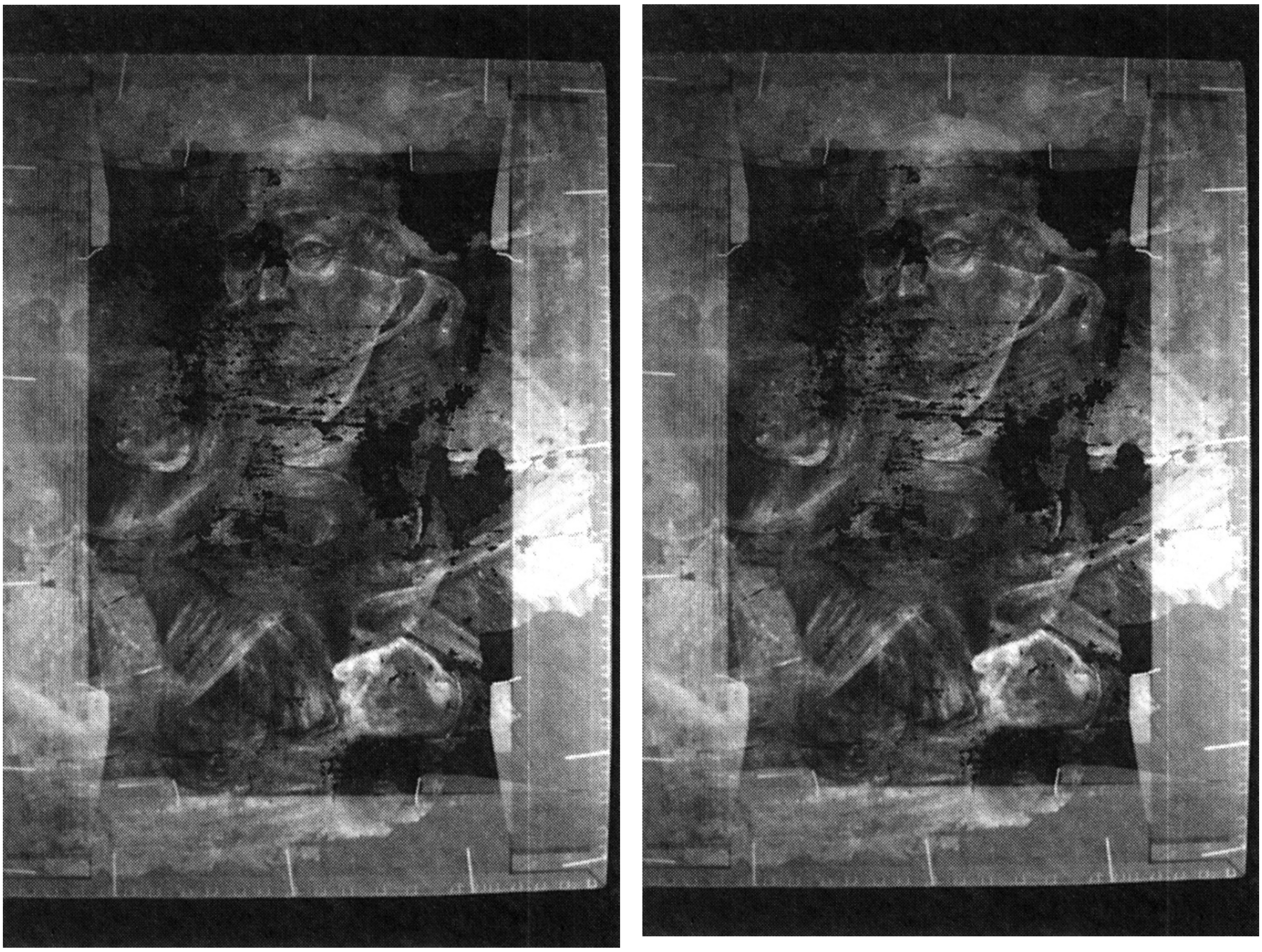

Fig.9-10 Mattia Preti, *San Pietro e San Paolo* xray immage

- The stratigraphic sections have shown for the works carried out in collaboration (Our Lady of Providence and Purity): mestica of yellow-brown color, applied in the fragments of greater thickness in two subsequent drafts, based on calcium carbonate and silicates and with the presence of small quantities of iron oxides; in different parts of the sample the pigment are typical of palette of the seventeenth century, but applied with different drafts; In parts made by Gregorio always is highlighted the presence of a background color based on lead white surmounted by a subsequent drafting of different color, while those realized from Mattia have a single paint layer (mixture of different types of pigments); Drafting film-forming surface (paint) in lumps, definitely restoration material infiltrated below the mestica

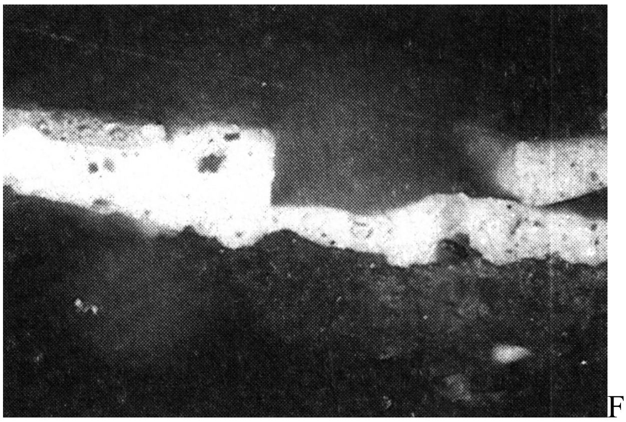

Fig.11 *Madonna della Purità stratigrafic section*

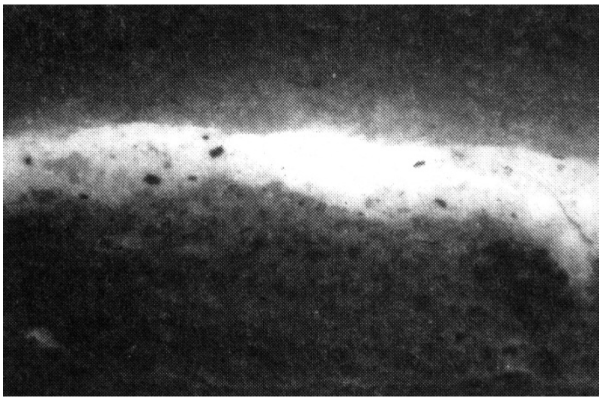

Fig.12 *Madonna della Provvidenza, stratigrafic section*

The analysis in stratigraphic section, the Preaching of St. John the Baptist and Saints Peter and Paul (attributed to Mattia Preti), reported the presence of a thick mestica different from the previous ones, consisting mainly of a bolus (reddish clay mineral); glazes crettate following phenomena contractive due to the high percentage of binder; drafting film-forming surface (paint restoration) penetrated into the underlying layers, visible in UV stratigraphic analysis.

In Jael kills Sisera analysis has shown the presence of a mestica orange brown of ochres red and brown with calcium carbonate and minor amounts of quartz and chalk. Thick paint layer, with the bottom base of white lead pigment and little pitch, overlooked by a further application with a greater amount of pigment. Drafting film-forming surface with paint restoration that penetrates deep into the cracks of the paint film and the mestica.

6.4 Conclusions

The analyzes have allowed us to recognize the Gregorio's and Mattia's characteristics of materials and stylistic . The main differences are:

Gregorio : No preparatory drawing,mestica gray-brown of calcium carbonate and silicates technical executive with brush strokes with different color to the background. Using color engraving for decorative details.

Mattia: Creation of detailed preparatory drawings, red preparation of bolus ,technical executive with long strokes and finishing glazes.

All information collected through scientific analysis,it has been to recognize, in an objective manner:any works currently attributed to Mattia Preti but mere stylistic imitation by his brother Gregorio that after the forty years of the seventeenth century began to "imitate" the art of Mattia (the paintings with Jaele for example)

- possibility to identify precisely in their collaborations, the parts paintend by Mattia and the parts by Gregorio.
- fundamental help to establish the authenticity of their works.

7. Conclusions

The aim of this thesis work was to develop Chemical- Physics methodology to date and characterize ancient artefacts.

- The first argument taken into consideration was the possibility to date wooden artifacts by using FTIR analysis.Twenty samples of wooden artifacts which dates from the fifteenth century and part comes to the twentieth century. In particular, the study of samples of poplar which is the essence most used for the construction of wooden sculptures have allowed to verify a great stability of the hypothesized relationship in this research work as correlative important than the age of the articles. Although the normalized value of the intensity of the spectral band of the carbonyl is slightly variable, it was possible to observe a good linear correlation between this data and the age of spectral artifacts. Unfortunately when the investigation went more wide we had to conclude that this method on dating wood artifacts is strongly limited by the chemical treatments used in the past to ensure their conservations. In particular old statues in the majority of cases have been dipped into
Resins bearing carbonyl groups: the same chemical groups which were hypothesized to be correlated to the age of the woods.

The second arguments taken into consideration was to ascertain the possibility to use optical and SEM (Electron Scanning Microscopy) to characterize and to date ancient icons. In Particular, the identification of repainting and refurbishment of two icons triptych from the Museum of Frascineto were studied. On the basis of this case study we could conclude that these two techniques are able to ascertain the country of origin of these artifacts. In The case of studied icons we could conclude that they had a common geographic origin even if their authors were different. A furter potentiality of these techniques is the possibility to discover the restoration processes occurred in the past.

A third research line concerns the potentiality of FTIR (Fourier transform Infrared Spectroscopy) and XRF (X ray Fluorescence Spectroscopy) to ascertain the conservative stage of ancient frescos and tio identify previous restoration intervention. In this case these two methodologies have been applied to elucidate a practical case: the study of arc decoration in the del Santuario di Santa Maria delle Armi di Cerchiara. We could identify both the original material used for the decoration (mainly gold) and the materials that have been used to restore them in past (porporin).

-The same techniques have been used to study the possibility to date ancient codex. In particular the potentialities of this methodologies have been tested on the characterization and dating of a manuscript for which has been proposed a dating on the late sixteenth century: The Romano Carratelly Codex. The XRF analysis brought to the identification of an iron gall ink made from an old recipe still not modified by in-depth studies in the seventeenth century. The materials and techniques used support a datation at the end of the sixteenth century.

Finally, several scientific methodologies have been used to verify the possibility to identify the authors of ancient paints. In particular , the works of the two artists: Gregorio and Mattia Preti have been studied by X Ray, SEM-EDX and IR spectroscopy, to attribute correctly paints for which the historical attribution to these authors was still under discussion. The analyzes have allowed us to recognize the Gregorio’s and Mattia’s characteristics of materials and stylistic .

The main differences are:

-Gregorio : No preparatory drawing,mestica gray-brown of calcium carbonate and silicates technical executive with brush strokes with different color to the background. Using color engraving for decorative details.

- Mattia: Creation of detailed preparatory drawings, red preparation of bolus,,technical executive with long strokes and finishing glazes. All information collected through our scientific analysis, brought to recognize, in an objective manner: any works currently attributed to Mattia Preti and also mere stylistic imitation by his brother Gregorio that after the forty years of the seventeenth century began to "imitate" the art of Mattia.

Bibliografia