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An integrated multi-analytical approach to the study of the dome wall paintings by *Correggio* in Parma cathedral

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ABSTRACT

The restoration of one of the most famous masterpieces of the Renaissance, the wall paintings regarding the *Assumption of the Virgin Mary* painted inside the dome of the Cathedral of Parma by Antonio Allegri called Correggio (1489–1534) between 1526 and 1530, allowed an in-depth chemical-physical study of materials. Non-invasive infrared imaging and spectroscopic techniques (reflectance spectrometry in the visible range and in-situ X-ray fluorescence) and micro-invasive analytical techniques (optical microscopy, scanning electron microscopy with energy dispersive X-ray microanalysis, powder X-ray diffraction, micro-FTIR spectroscopy, micro-Raman spectroscopy, and gas chromatography coupled with mass spectrometry) were chosen in order to provide the higher set of significant data, limiting as much as possible sampling. The joined use of different techniques allowed to deeply explore Correggio's palette, on the use of *a fresco* and/or *a secco* technique, to study as well degradation products and the diffused and old restoration materials like consolidants. The study allowed the characterization of a wide range of pigments, the identification of the binding media, mainly egg and animal glue, the restoration materials (acrylic resins, paraffin waxes, various pigments) and the degradation products (calcium sulfate dihydrate and calcium oxalate).

1. Introduction

From a chemical point of view, an integrated analytical approach based on the use of non-invasive and micro-invasive techniques is demanded to define painting materials and technique, the state of conservation and causes of degradation of the wall paintings [1,2]. A large set of analytical techniques, performed on the field and in laboratory, is not frequently provided, and generally only non-invasive or sampling methods are chosen. In particular, when large surfaces have to be examined, as for mural paintings, non-invasive tools must be reduced to portable ones and a specific protocol dealing with the most effective methods and timeline should be set in order to optimize the work to get better results.

A good protocol should normally follow this sequence, starting with non-invasive tests and then concluding with sampling [3,4]:

1. imaging analyses;
2. non-invasive spectroscopic analyses;
3. micro-sampling, useful for different kind of non-destructive or destructive exams.

About this last point, depending on the goal of the research, samples can be studied as they are or mounting cross-sections for microscopic and spectroscopic analyses, or destroyed to carry out chromatographic analyses.

The restoration of one of the most famous masterpieces of the Renaissance, the wall paintings regarding the *Assumption of the Virgin Mary* (Fig. 1) painted inside the dome of the Cathedral of Parma by Antonio Allegri called Correggio (1489–1534) between 1526 and 1530, allowed an in-depth chemical–physical study of materials.

In this case the above mentioned protocol was used, with the aim to obtain a characterization of the organic and inorganic components employed, including the stratigraphic sequence of the pigments and the organic binders. The objective was to elucidate the painting technique, the state of preservation, the possible decay processes and the possible additions made during previous restorations.

The scientific analyses were performed during the last recent campaign of restoration, following the previous one that took place in

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1970s. The goal was to offer the appropriate scientific tools for the design and the execution of an appropriate restoration intervention.

First, in order to collect as much information as possible by minimizing the sampling, a non-invasive *in situ* campaign was carried out using portable instruments. Imaging techniques like IR reflectography (IRR) and false color infrared (IRC), followed by spectroscopic ones, like reflectance spectrometry in the visible range (vis-RS) and X-ray fluorescence (ED-XRF), were chosen as informative first-step analyses. Then, after sampling, micro-fragments of the painting material were analyzed by several analytical techniques: optical microscopy, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), powder X-ray diffraction, micro-FTIR spectroscopy, micro-Raman spectroscopy, and gas chromatography coupled with mass spectrometry (GC-MS).

The study also enabled to extend the results obtained by chemical analyses on samples of the same wall paintings collected by the researchers of Opificio delle Pietre Dure in Florence in 1974–1975 [5] and to compare the new data with those obtained on other mural paintings of the same author, period and town [6,7].

2. Experimental

2.1. Samples

The following techniques were employed in the aforesaid sequence, mainly on the mural paintings belonging to the lower part of the cupola (apostles and ephebes, see Fig. 1).

A total of 26 samples (Table 1) were collected from the wall paintings, either by gently rubbing the color from the surface, or by detaching a small piece of the wall painting in to prepare the cross-sections according to current methodology [8].

2.2. Instruments and methods

2.2.1. Large area imaging examinations

IR reflectography (IRR) and false color IR (IRC) images were taken with different degrees of detail (from some m^2 to some dm^2) on many areas of the painted surface, to reveal discontinuities in the use of pigments inside apparently homogeneous chromatic zones [9].

The IRR and IRC images were obtained by a Sony digital camera with silicon CCD detector (9 Mpx), resolution above 10 pixel/mm, using an interference 850 nm high-pass filter and halogen lamp (1000 W) [10].

2.2.2. Reflectance spectroscopy (vis-RS)

The vis-RS measurements have been obtained using a handheld spectrophotometer Minolta CM 2600d spectrometer: 360–740 nm range, 10 nm acquisition step, integrating sphere included, UV source included, d/8 geometry, 3 mm diameter spot. This choice enables fast data acquisition and reliability in identifying spectra as tested on the field during many campaign of analyses on ancient and modern pigments [11], considering the typical broad bands of RS spectra and the little variability in the position of the features of the spectra (reflectance minima and shoulders) when pigment concentration changes, usually in the order of a few nanometers. RS instruments with higher spectral resolution (1 nm or lower) are usually not necessary to identify pigments. A wide personal reference database was used to interpret results, together with literature data.

2.2.3. Energy dispersive X ray fluorescence (ED-XRF)

XRF spectra were taken through a portable Bruker AXS ARTAX micro-XRF instrument, mounting a Silicon Drift Detector (SDD) and an air-cooled Mo X-Ray fine focus tube (max 50 kV, 0.7 mA, 30 W), equipped with a point collimation system, able to concentrate to a

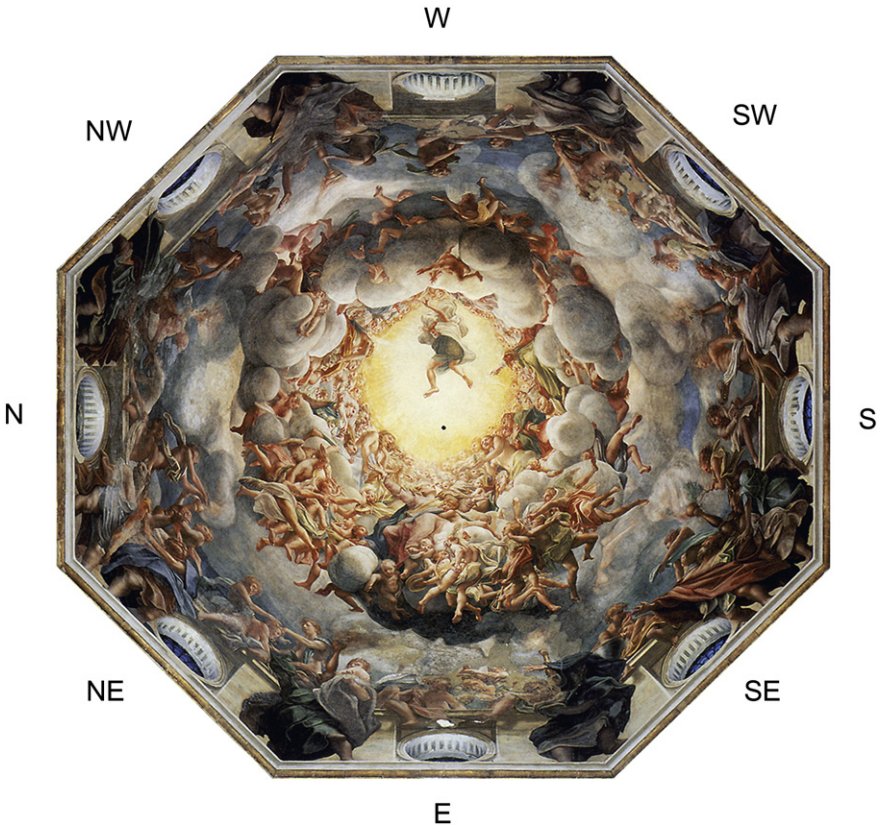

Fig. 1. A view of the inside walls of the cupola. The cardinal points are indicated.

Table 1
The samples collected and their description.

Sample	Position	Color	Description
1	South	grey	Light spot on grey
2	South	blue	Sky
3	North-east	pink	Skin of ephebe
4	North-east	white	Near red dress of apostle
5	South-east	grey	Dress of apostle
6	South-west	yellow	Dress of apostle
7	East	green	Dress of apostle
8	East	pink	Skin of apostle
9	South-east	red	Dress of apostle
10	East	green-blue	Dress of apostle
11	East	blue	Dress of apostle
12	North	white	Backdrop
13	North	blue	Sky
14	North-east	green	Dress of ephebe
15	East	yellow	Dress of ephebe
16	East	white	Sinopia
17	West	brown	Dress of apostle
18	East	dark	Dress of apostle
19	West	blue	Sky
20	West	blue	Sky
21	North-east	blue	Sky
22	North-east	blue	Sky
23	North-east	green	Dress of apostle
24	South-east	red	Dress of apostle
25	East	blue	Dress of apostle
26	North-east	blue	Sky

spot smaller than 70 μm diameter. Using the instrument's inner CCD camera and a laser pointer, the analyses were made on surfaces having a diameter of about 200 μm.

2.2.4. Scanning electron microscopy coupled with energy dispersive X-ray microanalysis (SEM-EDS)

SEM-EDS analyses were performed with a Jeol 6400 scanning electron microscope equipped with an Oxford (Link) EDS microanalysis system (15 kV, 0.28 nA, ~1 mm beam diameter, 60 s counting time). Elemental data were then obtained using the Oxfordb INCA-Energy software.

All the cross sections and the samples were analyzed by SEM, applying them on aluminum stubs by an Ag-conductive glue and obtaining a better conductivity through sputtering of approx. 8 nm of metallic gold on their surface (EMITECH K550 sputter coater).

2.2.5. Micro-Raman spectroscopy

Non-polarized Raman spectra were recorded at 632.8 nm (nominal 15 mW He-Ne laser excitation) in a nearly backscattering geometry with a Jobin Yvon LabRam micro-spectrometer (300 mm focal length spectrograph) equipped with an integrated Olympus BX40 microscope. The spectral resolution was about 1.5-2 cm^{-1}. The Rayleigh radiation was blocked by a notch filter and the backscattered Raman light was dispersed by an 1800 grooves/mm holographic grating on a Peltier cooled CCD, made by an array of 1024/256 pixels. The entrance slit width was fixed at 100 μm. The laser power was adjusted by means of a series of density filters to avoid any damage to the samples or uncontrolled thermal effects. The average power on the sample was always less than 3 mW. Spectra were collected using both 100× or long working distance-50× microscope objectives. Typical exposures were 10–60 s, repeated 3–5 times. The system was frequently calibrated using the 520.6 cm^{-1} Raman band of silicon or by means of reference emission lines of Ar or Cd light sources. The data analysis was performed by LabSpec built-in software. Raman spectra were collected in selected spots on the surface of the samples as well as on the cross-sections to analyze the composition of the different layers of painting [12].

2.2.6. Micro-Fourier Transform Infrared Spectroscopy (FTIR)

Micro-FTIR spectra were taken in attenuated total reflectance (ATR) mode employing a ThermoNicolet "Continuμm" Nexus line microspectrophotometer, equipped with a mercury–cadmium–telluride (MCT) detector. A micro-slide-on ATR silicon crystal directly connected to the objective has been used. Infrared spectra were recorded in 4000–650 cm^{-1} range, resolution 4 cm^{-1} and 120 scans. All spectra were collected on micro-samples and are presented in transmittance units after baseline correction.

2.2.7. X-ray diffraction (XRD)

Part of each sample has been finely ground by hand in agate mortar to be analyzed by XRD using a THERMO ELECTRON ARL X'TRA powder diffractometer. The instrument was equipped with a CCD, using MoKα (17,43 KeV) radiation, operating at 40 kV and 20 mA. The XRD data were collected from 5° to 75° 2θ with a step-size of 0.05°.

2.2.8. Gas Chromatography - Mass Spectrometry (GC-MS)

A Focus GC (Thermo Scientific) coupled to DSQ II (Thermo Scientific) with single quadrupole and split–splitless injector was used. The mass spectrometer was operated in the EI positive mode (70 eV). The carrier gas was used in the constant flow mode (He, purity 99.995%) at 20 mL/min.

2.2.9. Fatty acid and amino acid analytical procedures

The basic methodology relied on the identification of fatty acids and amino acids on the same sample. Two chromatograms were therefore collected for each sample: the first one from fatty acid derivatives, the second from amino acid derivatives. [13,14]. The internal standards considered were: heptadecanoic acid (50 μl of a 0.1 mg/ml solution w/v) for the analysis of fatty acids; norleucine (50 μl of a 0.1 mg/ml solution w/v), and norvaline (50 μl of a 0.01 mg/ml solution w/v) for the amino acids analysis; the analysis was conducted on 1 mg of paint samples. Separation of components was done by means of a fused-silica capillary column (RXI-5, Restek) with a 0.25 μm (30 m × 0.25 mm × 0.25 μm) methyl-silicone (5% phenyl) film and the injector was used in splitless mode. The sample was treated with 4 N-HCl in methanol (1 ml) and n-hexane (1 ml) for 2 h at 50 °C. The n-hexane phase, which contains fatty acid methyl-esters, was used for gas chromatographic analysis (1 μl). Separation of the methyl ester of fatty acids was achieved following this temperature program: isothermal conditions at 80 °C for 2 min, with 20 °C/min heating up to 280 °C and isothermal conditions at 280 °C for 6 min (total run time 18 min). The mass spectra were collected in Total Ion Current (TIC; 40–500 *m/z* fragmentation rate). After evaporation to dryness of the methanol phase, the residues were dissolved in 6N hydrochloric acid (2 ml) and hydrolyzed in a screw-capped container for five hours at 100 °C in an oil bath, under nitrogen atmosphere. After evaporation to dryness, the hydrolyzed residues were esterified using 3 ml of 2N HCl in propan-2-ol at 90 °C for one hour. After cooling, the solvent was evaporated under vacuum and the residue of the paint was dissolved in 0.2 ml of dichloromethane and derivatized with 0.2 ml of trifluoroacetic anhydride at 60 °C during one hour. After cooling, the solvent was evaporated under vacuum and the residue of the paint sample was dissolved in 0.2 ml of dichloromethane, then the solution was used for gas-chromatographic analysis (1 μl). Separation of N-trifluoroacetyl-O-2-propyl esters amino acids derivatives was achieved following this temperature program: isothermal conditions at 60 °C for 3 min, with 25 °C/min heating up to 260 °C and isothermal conditions at 260 °C for 6 min (total run time 17.00 min). The mass spectra were recorded in Selected Ion Monitoring (SIM; 140, 126, 154, 153, 139, 168, 182, 166, 164, 184, 180, 198, 91, 190 *m/z* fragments). A qualitative analysis was performed in order to identify lipids and proteins contained in the painting, and the average amount of fatty acids and amino acids relating to the internal standards was considered.

2.2.10. Fatty acids, alcohols, and hydrocarbons procedure

Samples (500–1000 μg) were hydrolyzed with 5% KOH (1 ml) in methanol by vigorous stirring 60 min at 80 °C and extracted twice,

after cooling at room temperature, with hexane (2 ml). The hexane extract (neutral fraction), transferred in a closed conic vials, was admixed with 1 ml standard solution of N-eicosane (internal standard, 500 ppm in hexane). Then, the mixture was acidified with 1 ml hydrocloridric acid (6N) and extracted twice with 1 ml of diethyl ether (acid fraction). The extracts were put either in a screw cap test tube, dried under a gentle flow of nitrogen and submitted to trimethylsilylation with 100 μl *N*, *O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The reaction was performed at 60 °C for 30 min. A 1 μl volume of the derivatized solutions was analyzed. Mass spectra were acquired in the scan range 40–500 *m/z*. The MS transfer line temperature was 280 °C; the MS ion source temperature was kept at 230 °C. The gas chromatographic separation was done in a DB5 fused-silica capillary column, 5% diphenyl–95% dimethylpolysiloxane, 30 m × 0.25 mm id, 0.25 μm, film thickness, (J&W Scientific, Agilent Technologies, Palo Alto, CA). The PTV injector was used in split mode at 280 °C. The chromatographic oven was programmed as follows: 80 °C, isothermal for 2 min, 10 °C/min up to 200 °C, 200 °C, isothermal for 5 min, 20 °C/min up to 280 °C, 280 °C, isothermal for 20 min.

3. Results and discussion

Energy dispersive X-ray fluorescence (ED-XRF) and visible Reflectance Spectroscopy (vis-RS), carried out on about 100 measurement points, were performed after the execution of IRR and IRC exams, and followed by sampling. Samples were chosen among areas suspected to present chromatic alterations (fading, darkening, etc.) or structural alterations (cracking, detachment, etc.).

3.1. Pigments

3.1.1. Blue pigments

Many points investigated by non-destructive techniques were chosen in the areas representing the sky and the dresses of apostles and ephebes.

A smalt blue pigment was identified by vis-RS through the typical absorption bands at about 530, 600 and 630–640 nm (Fig. 2) [15]. This occurred mainly in the areas depicting the sky. Smalt blue is an artificial potassium-glass where the blue color is due to the presence of cobalt [16]: it is used as a pigment since at least XIV century, and since XVI century in mural paintings [17].

XRF analysis confirmed this identification owing to the presence of Co (Kα at 6.93 keV, Kβ at 7.65 keV), As (Kα at 10.53 keV, Kβ at 11.73 keV) and Bi (Lα at 10.76 keV, Lβ at 13.00 keV, Lγ at 15.25 keV). As and Bi are common impurities in cobalt minerals, used to color the glass.

In the case of smalt-blue the micro-Raman spectroscopy cannot give a contribution because of strong fluorescence signal of cobalt ions in the glass and the absence of characteristic vibrational features to be assigned to cobalt oxides.

Only in some areas of the sky, where the XRF spectrum gives Cu characteristic lines, the micro-Raman spectra gave evidence of azurite [$Cu_3(CO_3)_2(OH)_2$] through the typical features at 245, 277, 396, 761, 830, 930, 1093 cm^{-1} (Fig. 4). This copper carbonate pigment usually used *a secco*, with organic binders of different nature (see next paragraph). XRD results on sample 11, collected in the south wall, also indicate azurite, together with the white calcium carbonate ($CaCO_3$), mainly belonging to the plaster, and gypsum ($CaSO_4 \cdot 2H_2O$). The latter could be found in the plaster, but often is due by sulphatation process, as discussed in the following. The XRD spectra show a strong background noise probably due to blue smalt pigment that, as glass, gives broad diffraction pattern. Moreover, in the areas of the sky, lazurite mineral [$(Na,Ca)_8((SO_4,S,Cl)_2|(AlSiO_4)_6]$, the main component of ultramarine blue (lapis lazuli), has been identified. Raman analysis carried out on cross-sections shows that ultramarine blue is located only on the surface (Fig. 3).

Vis-RS analysis did not identify this pigment, usually well detectable by its strong large absorbance around 600 nm due to its scarce presence in comparison to smalt. The expensive lapis lazuli was perhaps used only in thin layer (glazing) to achieve a better uniformity in the surface color, and its use *a secco* was most likely subjected to a larger damage during past cleanings.

Blue areas of the fresco depicting clothes are characterized by widespread use of azurite.

Through the IRC images (Fig. 4) it easily evidenced the distribution of this pigment on the surface by the dark blue-violet coloration, while red-pink areas refer to smalt blue (predominant, in this case) or to ultramarine blue [4].

The presence of azurite was confirmed by vis-RS, showing the typical absorption band at about 640 nm. Micro-Raman spectroscopy further confirmed the presence of azurite in dresses, mixed with ultramarine blue in the surface layers.

Raman spectra gave also evidence of hematite (Fe_2O_3), showing main peaks at 224, 290, 299 and 408 cm^{-1} [18], in the blue areas

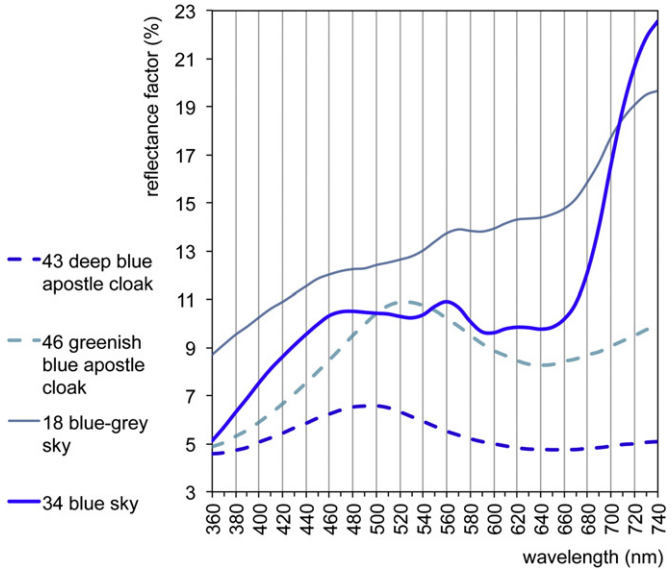

Fig. 2. Vis-RS spectra of blue areas characterized by smalt blue (solid lines) or by azurite (dotted lines). The spectrum of pale blue or grey-blue of some areas of the sky (curve 18) has lost its typical maximum in the blue region (440–500 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

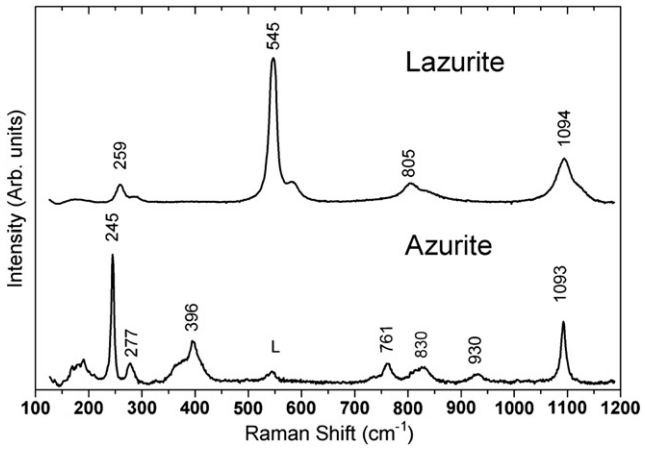

Fig. 3. Representative Raman spectra collected in blue areas showing the presence of lapis lazuli and azurite.

Fig. 4. Visible (a) and false color IR (b) details of the apostle in the East/South-East corner. The pink areas of the sky in IRC image correspond to the presence of smalt blue whereas the dark blue-violet ones of the cloak to the presence of azurite. Retouching with modern materials is evident. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

depicting clothes: here, an abundant presence of iron compared with other zones was confirmed by XRF analysis. The occurrence of this red pigment reveals a peculiar pictorial practice, sometimes used in the past [6,7], consisting mixing red ochre and azurite to improve color saturation.

Different shades of green have been used in the fresco. Cu is identified by XRF in some green areas, indicating copper pigments as malachite [$Cu_2CO_3(OH)_2$] or copper II acetate. Vis-RS does not help in the identification, which would have been possible only extending the range to near-IR.

Micro-Raman spectroscopy shows a diffuse presence of green earth pigment (mainly celadonite $K(Mg,Fe^{2+})(Fe^{3+},Al)[Si_4O_{10}](OH)_2$), identified by the typical bands at about 174, 202, 279, 393, 544 and 701 cm^{-1} [19], and confirmed by cross-section analysis. Raman spectra were also useful in the identification of hematite. As for blue hues, frequently in the past the dye was obtained applying a pigment on a layer of complementary color to improve the saturation and brightness. For example, sample 23 collected from a green area depicting a dress in the northeast wall shows a red layer of hematite under the layer of green earths (Fig. 5).

3.1.2. Yellow and brown pigments

The palette of yellow, yellow-orange and brown in the Correggio fresco is characterized by the use of yellow ochre or earths. XRF analysis shows the presence of Fe and vis-RS spectra always exhibit a small band at about 450 nm, related to the electronic transitions typical of Fe^{3+} ions arranged in octahedral symmetry that is characteristic of the iron oxides. The shape of the RS spectra, with an inflection point at about 550 nm, suggests a major contribution of yellow ochre (goethite) than the red one (hematite) (Fig. 6) [20].

Moreover, micro-Raman results identify goethite and hematite mixed with calcium carbonate and dark carbon to create different hues.

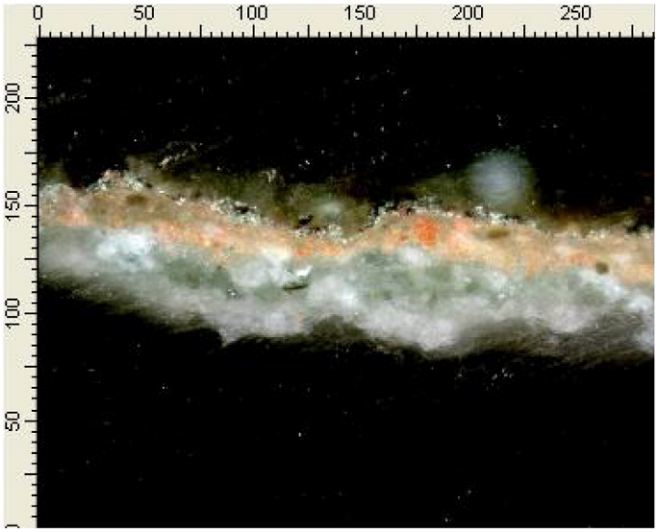

Fig. 5. Cross-section of sample 23, showing a red layer of hematite under a layer of green earths. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

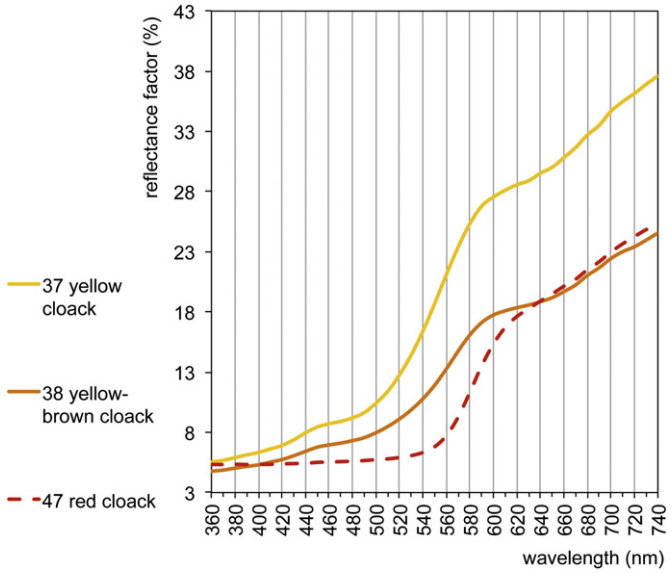

Fig. 6. Vis-RS spectra of yellow ochres (solid lines) and red ochres (dotted line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.1.3. Red pigments

Red pigments have been analyzed in the dresses and in the flesh tones of the characters represented in the painting. Hematite and vermilion (HgS) mixed together were identified in the dress areas by the different analytical techniques.

In particular, vis-RS curves with an inflection point at about 570–580 nm indicate the presence of iron oxides-based pigments (Fig. 6), i.e. red ochre (hematite), while the strong S-shape behavior is due to vermilion. The presence of iron has been confirmed by XRF and EDS analysis, whereas Hg has been identified by EDS. Micro Raman spectra further confirm the presence of cinnabar (253, 284 and 343 cm^{-1}) and hematite. In particular, the analysis performed on cross-sections gives evidence of cinnabar applied on a thick layer of hematite.

A different pigment mixture characterizes the areas representing the skin tones. No trace of cinnabar has been found and the pink-red color was obtained only by iron oxides based pigments (hematite), mixed with white calcium carbonate ("bianco di san Giovanni") to lighten the pigment. The signal of Pb, detected by XRF, indicates also a lead based pigment, like lead white, minium (Pb_3O_4) or litharge (PbO): not compatible with fresco technique they usually indicate in mural paintings the use of a secco painting. Some Pb count is also found in green and blue areas.

A different pigments mixture characterizes the areas representing the skin tones. No trace of cinnabar has been found and the pink-red color was obtained only by iron oxides pigments (hematite), mixed with calcium carbonate white ("bianco di san Giovanni") to lighten the pigment. The signal of Pb, detected by XRF in some reds (Fig. 7), indicates also the existence of a lead based pigment, like lead white, minium (Pb_3O_4) or litharge (PbO): not compatible with fresco technique they usually indicate in mural paintings the use of a secco painting. Not negligible Pb signals were also found in green and blue areas.

3.1.4. White and grey pigments

White and grey areas have been obtained by mixing calcium carbonate and other pigments (ultramarine blue, smalt blue, red and yellow ochre, black carbon) to obtain the different tones.

In the grey-purple clothes, for example, the comparison between vis-RS spectra and those obtained with simulated combinations of spectra of single pigments according to the Kubelka–Munk theory indicates a mixture of smalt blue pigment and red ochre (Fig. 8). In order to take into account possible alterations and peculiar hues, the reference pigments used for the simulated mixtures — red ochre and smalt — were taken from areas of the same mural painting where each pigment appears to be pure, apart from a mixture with white pigment. In this way one can simulate, in a first approximation, the same ageing effects that cannot be reproduced with commercial reference pigments.

The mixing between smalt blue and ochre found in wall paintings to obtain violet-grey colors can be considered a variation of the typical mixture between azurite or ultramarine blue and red lakes preferred for the same purpose by Correggio in the panel paintings.

The present analyses allowed to recognize a definitely larger palette in respect to those indicated in the reports dated 1975 [5], in which only smalt blue, azurite, calcium carbonate and single cases of basic copper carbonate and "probably madder lake" are cited.

3.2. Organic binders

The FTIR spectra of samples 19, 20 22, 23 and 25 show typical bands of proteinaceous material, i.e. the characteristic CH stretching at 2924 and 2954 cm^{-1}, C═O stretching of amide I at 1643 cm^{-1} and N – H bending of amide II at 1539 cm^{-1}. Based on these first indications gas chromatography coupled with mass spectrometry detector was used to identify the lipidic and proteinaceous materials.

Samples collected from blue (samples 19–22, 25, 26), red (sample 24) and green (sample 23) areas have been investigated through GC-MS. Three samples (21, 24 and 26) do not show relevant signal connected to amino acids or fatty acids excluding the presence of lipidic or proteinaceous binders.

Lipidic fraction gas chromatograms of the samples 23 and 24 are characterized by weak peaks of saturated fatty acids (palmitic and stearic acids), and oleic acid. These fatty acids are due to the lipidic fraction of egg.

Chromatograms of samples 19, 20 22, 23 and 25 show the amino acids signal (Fig. 9). To identify the binding media, the percentage content of amino acids in each sample was compared to those from a dataset of 43 reference samples of egg (whole, egg yolk, egg white), casein and animal glue, belonging to the reference collection of the Opificio delle Pietre Dure of Florence [21]. Principal component analysis (PCA) was performed on the correlation matrix of the relative percentage contents of eight amino acids (alanine, glycine, leucine, proline, hydroxyproline, aspartic acid, glutamic acid, phenylalanine) components [22].

The evaluation by means of PCA, whose score plot is reported in Fig. 10, locates all the samples in a new cluster suggesting a mixture of animal glue and egg binders.

The results indicate that samples 20, 22 and 25, in which azurite has been identified, are characterized by egg and animal glue as binder. However, the identification of the same combination of binders in samples 19 and 23, characterized by the presence of lapis-lazuli, smalt blue and green earths, allows to hypothesize the use of *a secco* technique also with pigments that do not require the use of binders. Observations made by researchers of Opificio delle Pietre Dure (Florence) in 1970s, using optical microscopy and spot tests on cross sections, indicated that "the paintings are not executed using the *buon fresco* technique, but tempera", and this result was confirmed on the same materials by researchers of Istituto Centrale del Restauro (Rome) [5]; binder was said to be "possibly egg." Their conclusion, based only on a small number of samples (about 10), was quite hazardous, but is substantiated by our analyses on a similar number of samples, using more refined analytical tools.

3.3. Restoration and degradation materials

The ATR FT-IR analyses revealed in sample 22 (blue area of the sky, in the NE wall) and in sample 23 (green fabric in the NE wall) the

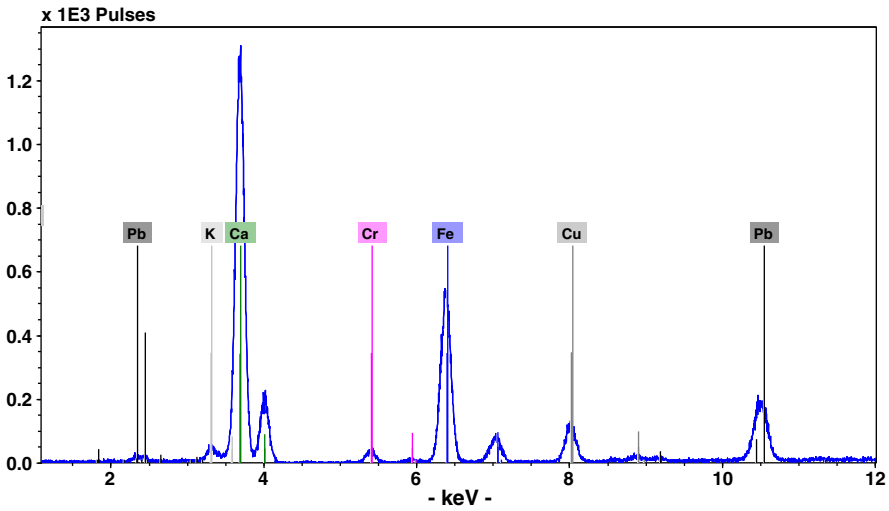

Fig. 7. ED-XRF spectrum of a skin area. Ca, Fe and Pb signals are evident. Cr and Cu are also present.

presence of Acrylic resins, Paraloid™ like (Fig. 11). This consolidator/protective is widely used from a long time in wall paintings restoration. Here, this synthetic compound seems to have been used mostly on blue and green areas.

In samples 21 and 26 (sky of the NE wall), 2 (sky blue in S wall) and 7 (green fabric in E wall), the micro-Raman spectroscopy revealed TiO_2, white pigment used after 1920 only; thus was confirmed by the presence of Ti in XRF. Samples 10 (blue fabric in E wall), 13 (sky blue in N wall), 23 and 7 (green fabric in E wall), and 14 (green fabric in NE wall) show, in Raman spectroscopy, confirmed by XRF, the presence of Cr oxides. Moreover, in samples 20 (sky blue in W wall) and 15 (yellow fabric in E wall) Raman spectroscopy revealed the presence of compounds belonging to the family of Cu phthalocyanine, organic dyes not present before 1935. In sample 15, XRF found a big amount of Chlorine, often present in such dyes.

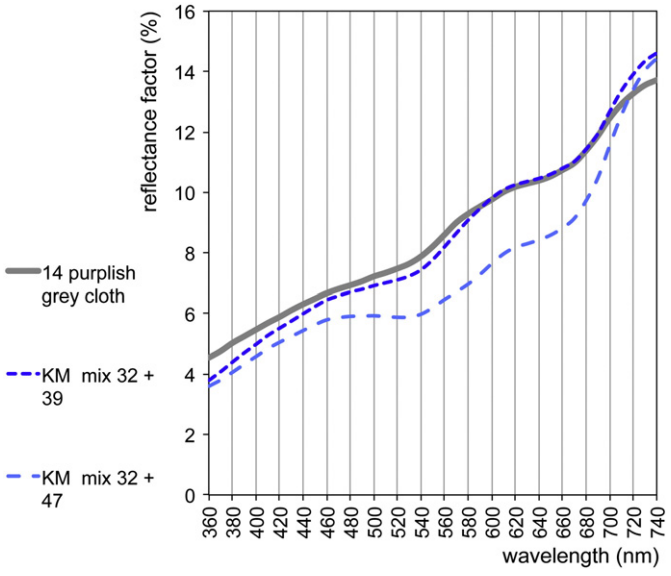

Fig. 8. Vis-RS spectrum of a greyish area (solid line) compared to spectra of simulated Kubelka-Munk mixtures (dotted lines) of smalt blue with a red ochre (lower curve) or with a yelloy-brown ochre. The spectra used in simulation are acquired on different points of the same painting. The similarity between these mixtures and the measured spectrum (14) suggests the grey color is obtained with a similar mixing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The attempt to find and recognize organic molecules, like fatty acids, alcohols and hydrocarbons, was made by means of GC-MS on samples 9 (red fabric in SE wall), 10 (blue fabric in E wall) and 14 (green fabric in NE wall). The results show the presence of odd and even hydrocarbons molecules, and the presence of Palmitic and Stearic Acids. The long-chain alcohols absence let us exclude the presence of natural waxes, like bee's wax, whilst was found the evidence of artificial waxes, like paraffin. Most of the analyzed samples by micro-Raman technique showed the presence of Gypsum ($CaSO_4$ $2H_2O$), by the bands at 414 cm^{-1}, 1007 cm^{-1} and 1132 cm^{-1}. Gypsum is formed by the reaction of Calcium Carbonate with Sulphuric Acid, formed by the oxidation of SO_2 and SO_3, easy to find in urban areas. In many samples also Calcium Oxalate was found, probably due to the oxidative degradation of organic compounds that were applied on the surface, to protect or to consolidate it.

4. Conclusions

The restoration of the most famous work of art in Parma cathedral, the *Assumption of the Virgin Mary* by Correggio, allowed to experiment the combination of many non-invasive and micro-destructive techniques to assess the correct analytical procedure for the study of this wall painting.

The followed protocol allowed the identification of the materials used and revealed significant details about the painting technique, minimizing the sampling of the artwork. In fact, it was possible to characterize a wide range of pigments, to identify the binding media and to recognize restoration materials (acrylic resins, paraffin waxes, various pigments) and degradation products (calcium sulfate dihydrate and calcium oxalate).

It is important to point out that the use of a single technique, or of a limited subset of technique, would lead to a failure in the detection of some compounds, especially where mixed pigments and dyes were used. Different techniques could lead to different conclusions. For example, in the blue area, smalt was nearly invisible in Raman spectroscopy, while the small amount of ultramarine blue was not revealed by vis-RS analysis. And organic dyes, such as copper phtalocyanines, are not detectable by XRD and XRF, but through Raman or vis-RS. In this case, only small amounts of copper could be revealed by XRF, impossible to distinguish from the signal coming from azurite or other Cu-containing pigments.

In our case, the use of visible reflectance spectroscopy, ED-XRF, SEM/EDS, Raman and FTIR spectroscopies and GC/MS allow to consider complete the presented results. In particular, the painter's palette resulted

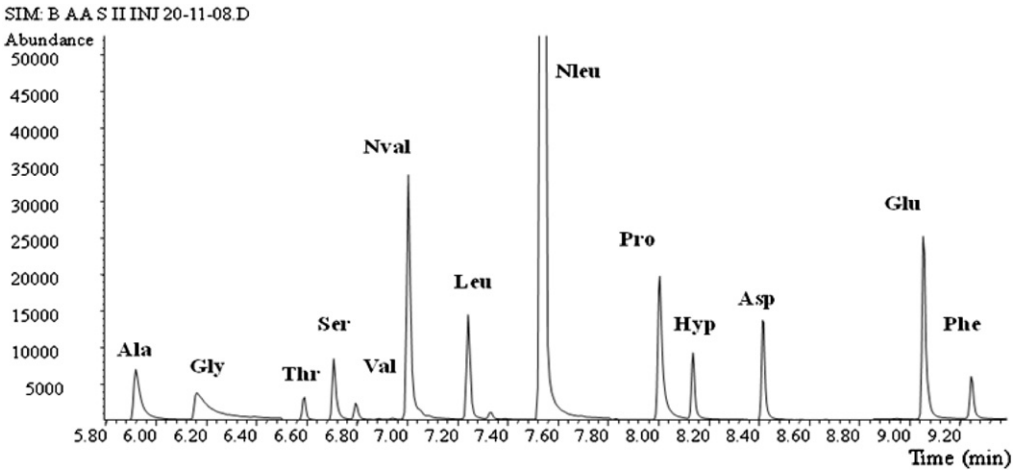

Fig. 9. Chromatogram of the proteinaceous fration of sample 20. Ala = alanine, Gly = glicine, Thr = threonine, Ser = serine, Val = valine, Nval = norvaline (internal standard), Leu = leucine, Nleu = norleucine (internal standard), Pro = proline, Hyp = hydroxyproline, Asp = aspartic acid, Glu = glutamic acif, Phe = phenylalanine.

composed by mineral pigments, sometimes expensive such as lapis lazuli, azurite and cinnabar, together with a wide range of earths, as well as some synthetic ones like smalt blue.

A rich use of organic material as binder media was found in the painting. In addition to the proteins (mainly egg and animal glue) originally used by the painter, some organic materials employed in restoration processes were detected, in particular acrylic resin.

The results of FTIR, GCMS and optical observations of the samples allowed identifying the abundant use of *secco* pictorial technique instead of the supposed fresco that appears to be used only for some under-layers and grounds. Also the presence of lead containing pigments in many colored zones refers to *secco* technique. Correggio used to work as for common fresco paint, with small fresh areas of plaster, called working days, which are around 283 for the entire dome, allowing to accurately consider the underlying drawing obtained by proper cartoons (sinopia) to guide him during the execution. However, over this fine plaster he made only a limited use of fresco painting, preferring to use pigments in tempera, which permitted to prolong the time of execution and to obtain better details and finishing.

The scarce use of carbonated pigment and the wide use on the walls of tempera can be considered a factor that enhanced the degradation of the pictorial cycle.

The coupled use of non-invasive and micro-invasive analyses shows great potential for disclosing the pictorial technique and to identify a wide range of materials, minimizing the potential damages to the opera and offering a decisive extension to traditional chemical methods.

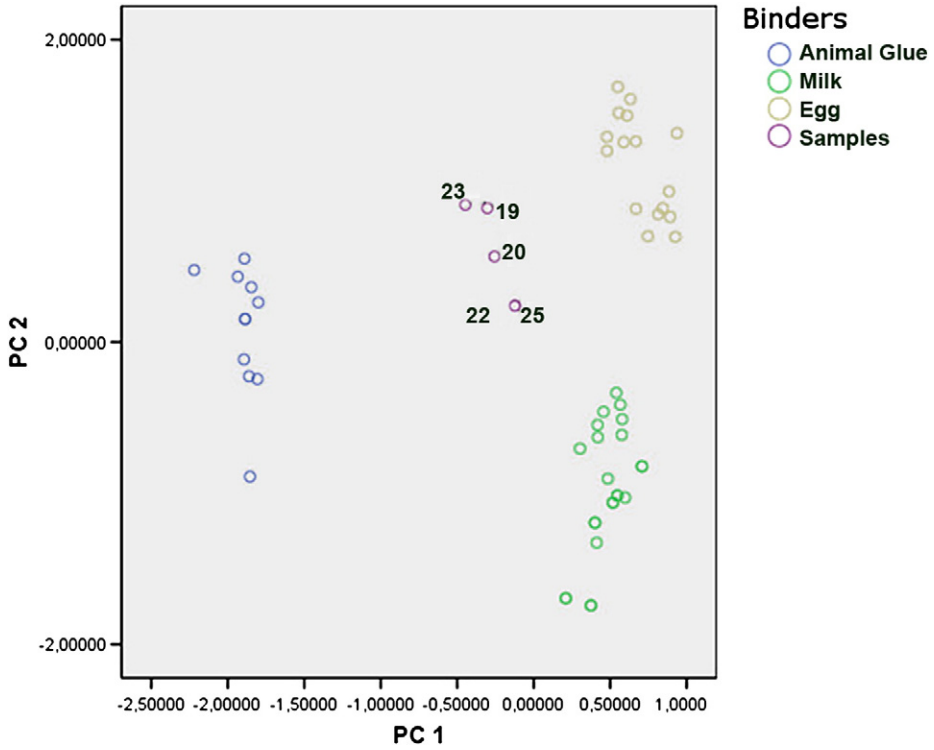

Fig. 10. Score plot of reference materials and wall painting samples (blue circle: animal glue; green circle: milk; yellow circle: egg; purple circle: samples). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

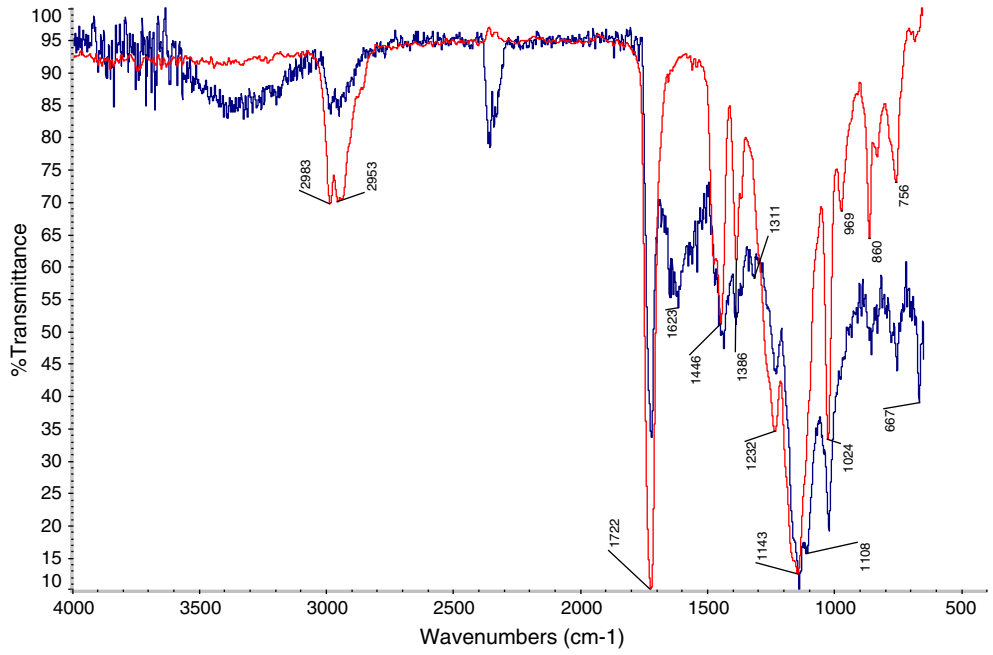

Fig. 11. FTIR spectra of sample 23 (blue line) and of acrylic resin Paraloid (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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