Appl Phys A (2013) 113:1055–1064
DOI 10.1007/s00339-013-7748-6

Applied Physics A
Materials Science & Processing

A scientific approach to the characterization of the painting materials of Fra Mattia della Robbia polychrome terracotta altarpiece

M.L. Amadori · S. Barcelli · A. Casoli · R. Mazzeo · S. Prati

Received: 19 April 2013 / Accepted: 30 April 2013 / Published online: 22 May 2013

Abstract During the last restoration (2008–2011) of the polychrome terracotta altarpiece called *Coronation of Virgin between Saints Rocco, Sebastian, Peter martyr and Antonio abbot*, located in the collegiate church of S. Maria Assunta in Montecassiano (Macerata, Italy), scientific investigations were carried out to acquire detailed information about the painting technique. The identification of materials allowed a correct restoration.

The altarpiece is almost entirely realized by Marco della Robbia (Fra Mattia), dates back to the first half of the XVI century and represents an interesting example of painted terracotta produced by using two different techniques: glazed polychrome terracotta and the "cold painting" technique.

The characterization of the samples' material constituents was obtained by analysing the cross-sections and the fragments by different techniques (optical, SEM-EDS and ATR-FTIR microscopy as well as GC-MS), as the real nature of a component is often difficult to assess with one single technique.

The optical microscope examination of paint cross-sections shows the presence of many layers, indicating the complexity of the paint stratigraphic morphologies. The original polychromy of della Robbia's masterpiece is constituted of cinnabar, red lake, red lead, orpiment, red ochre, lead white, lead tin yellow, green earth and raw umber. Two different types of gilding technique have been distinguished. The first one presents a glue mordant, and the second one shows an oil mordant composed by a mixture of red lead, red ochre, cinnabar and orpiment. The GC-MS analysis allowed the characterisation of linseed oil and a mixture of animal glue and egg as binding media stratigraphically located by the use of ATR-FTIR mapping microscopy. The analytical results of the painted terracotta integrated investigations show that original technique adopted is characterised by the application of pigments in an oil-binding medium directly applied on the substrates, probably treated with oil and animal glue.

A large number of overpaintings above the original scheme of polychromy was found, which could be ascribed to almost three different interventions; the absence of modern pigments suggests that they could be realized long ago.

1 Introduction

Despite the wide number of studies carried out on della Robbia's glazed artefacts [1–3], the scientific characterisation of the technique adopted to paint terracotta artefacts has received few attentions so far [4].

The restoration intervention of the terracotta altarpiece located in the collegiate church of S. Maria Assunta in Montecassiano (Macerata, Italy) offered the opportunity to study for the first time this uncommon *secco* technique used by the artist, filling a knowledge gap.

The big altarpiece called *Coronation of Virgin between Saints Rocco, Sebastian, Peter martyr and Antonio abbot* (Fig. 1) is almost entirely realised by Marco della Robbia

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M.L. Amadori (✉) · S. Barcelli
Department of Basic Sciences and Fundamentals, University "Carlo Bo" of Urbino, P.za Rinascimento 6, 61029 Urbino, Italy
e-mail: maria.amadori@uniurb.it

A. Casoli
Chemistry Department, University of Parma, V.le G.P. Usberti 17/a, 43124 Parma, Italy

R. Mazzeo · S. Prati
Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL), University of Bologna, via Guaccimanni 42, 48100 Ravenna, Italy

Fig. 1 Della Robbia altarpiece in S. Maria Assunta in Montecassiano (Macerata, Italy) after restoration

(Fra Mattia) and represents the only work of the "Florentin artist pottery", certainty attributed to him [5–7]. Even if a formal contract has not been discovered, it is documented that the Community of Montecassiano committed the decoration of the main altar to Fra Ambrogio and Fra Mattia, around 1527. The realisation of the altarpiece began again in April 1529, and Fra Mattia himself concluded the work between 1530 and 1532 [8].

Fra Mattia was certainly not a great plastic sculptor, but his capacity to innovate the stylistic and technical constructive module of the old *robbiane* repertory, by developing more pictorial, complex compositions, is well known and appreciable in the artworks under investigation.

In the big lunette the eternal Father between the angels is situated. The *Virgin* with *Child* is represented in the upper section of the altarpiece, hanging among clouds, crowned by two angels. In the area below the two bas-relief figures of *Peter martyr* and *Antonio* abbot are disposed in a pyramidal composition, and, in foreground, the almost full relief figures of *S. Sebastian* and *S. Rocco* are visible.

In the eighteenth century an earthquake damaged this monumental altarpiece, and therefore it was disassembled and restored when the church was repaired and enlarged; later on it was reassembled on the wall of the right aisle of the church. Such interventions interested the pictorial layers too, and therefore they were overpainted several times.

The Montecassiano altarpiece presents decorative and technical solutions similar to the one adopted for the San Francesco altarpiece, realised in Macerata by Fra Ambrogio and today missing. A document, related to the realisation of that altarpiece contains detailed iconographic and technical recommendations about the execution technique to be applied [8]. In particular, the executors were obliged to paint the figures by using an oil painting technique, while the other parts of the artefact have been realised in glaze terracotta [9].

The use of a mixed technique was certainly not only due to economic reasons; painting was in fact less expensive than glazing, but probably painting allowed improving the representation of natural elements better than glazing. Glazed terracotta sculptures, with oil painted parts, have been also realised by Andrea and Giovanni della Robbia [10–12]. It is worth mentioning that oil presence as binding medium is documented in different terracotta masterpieces [13, 14] as suggested by Gaurico in 1504 [15].

Thanks to a new restoration plan carried out from 2008 to 2011, the altar was disassembled again, and afterwards it was reassembled in a metallic structure. So it was possible to recognize that it presents a surface of about twenty-four square metres (4.20 m of base, 6.82 m high and 40 cm depth) made with a total of two hundred and sixty-two pieces. Most of the altarpiece consists of glazed terracotta, while approximately 30 % is composed by polychrome terracotta painted after all the pieces had been walled up without any preparation.

Usually before applying the painting layers, the terracotta surface was smoothed by a preparation of gypsum and animal glue [16, 17] followed by a priming made of oleoresin mixture or animal glue, or lead white and oil [11], or red ochre and red lead or lead white, red lead, yellow ochre with oil, or by a pink preparation made by gypsum and *chamotte* with a lead white and oil priming [13].

In order to acquire new information concerning painting technique and materials used by Fra Mattia, a preliminary scientific project was performed. Furthermore, the identification of original layers and overpainting permits to plan an appropriate intervention of restoration.

The present paper is focused on the possibility of approaching the above-mentioned questions using complementary and integrated scientific techniques, such as optical microscope, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy with energy dispersive X-ray microanalysis (SEM-EDS) and gas chromatography/mass spectrometry (GC-MS).

The stratigraphic investigations represent the most widely used techniques to identify the different layers applied on a substrate. Vibrational spectroscopy provides information about the molecular composition of material and has been used extensively for the identification of pigments. SEM-EDS provides elemental and morphological information. GC-MS method allows identifying and quantifying drying oils and presence of proteinaceous materials.

By employing all these techniques to representative samples a detailed set of data was obtained and compared with the literature ones, which will provide a complete understanding of the Montecassiano altarpiece.

2 Experimental

2.1 Sampling

Twelve micro paint fragments (Table 1) representing the colours were collected during the disassembly of the altarpiece and submitted to investigation. Before any analytical treatments, all samples have been documented using a stereomicroscope (binocular stereomicroscope Leica MZ6, 60×).

2.2 Preparation of cross-sections

All the samples have been embedded in a polyester resin support (SeriFix resin, Struers), then cross-sectioned and submitted to wet polishing with conventional methods using silicon carbide cards with successive grid from 120, 400, 800 to 1000. A second fragment of the samples MCR3, MCR9, MCR12 and MCR13 has been embedded in KBr in order to avoid the contamination caused by the polyester resin [18]. KBr cross-sections were prepared with the use of a macro–micro pellet die. First, KBr powder was pressed into the pellet under low pressure (2 t for 1 min) in order to achieve a soft base where to transfer the multi-layer fragment. The paint fragment was then positioned with the surface parallel to the base, and other KBr powder was added on. After a second, low-pressure application (3 t for 4 min), the pellet (13 mm × 3 mm) was extracted and transversally dry-polished using a specifically developed brass holder and silicon carbide cards with successive grid from 800, 1000, 2400 to 4000. The cross-sections have been submitted to different analytical investigations.

Table 1 List of samples and their location

Paint colour	Sample	Location
Red	MCR1	Robe of God
	MCR8	Robe of Virgin Maria
	MCR12	Mantel of Saint Rocco
Pink	MCR4	Left arm of an angel
	MCR11	S. Sebastian, drop of blood
	MCR20	Arm of an angel
Green	MCR9	Bust of an angel
	MCR13A	Robe of an angel
	MCR22A	Leaves of the tree at the top left
Grey Gilding	MCR2	Hair of God
	MCR3	Lunette
	MCR13	Wing of the angel

2.3 Optical microscopy

Dark field observations have been performed using an Olympus BX51M optical microscope equipped with fixed oculars of 10× and objectives with different magnifications (5, 10, 20, 50 and 100×). Visible and ultraviolet lights were provided by a 100 W halogen projection lamp and an Ushio Electric USH102D lamp, respectively. The microscope observation under UV light is commonly used as a first tool to qualitatively detect and stratigraphically locate the presence of organic materials (binding media, varnishes, etc.) thanks to the fluorescence effects generated by such materials when submitted to a UV radiation source. Cross-section photomicrographs were recorded with an Olympus DP70 digital scanner camera directly connected to the microscope.

2.4 Scanning electron microscopy and energy dispersive X-ray spectroscopy

A Cambridge Stereoscan 360 (Leika, UK) scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) by Link Analytical Oxford (Link, UK), model 6103, has been used on the same cross-sectioned samples already prepared for the optical microscope observations. A series of analyses have been made on each layer of the cross-sections. The elemental composition was carried out at acceleration voltage 20 kV, live time 40 seconds and working distance 30 mm.

2.5 FTIR spectroscopy

A Nicolet Nexus 5700 spectrometer combined with a Thermo Continuum IR microscope has been employed in these experiments. The system is fitted with a mercury–cadmium–telluride (MCT) detector cooled by liquid nitrogen and an X–Y–Z motorised stage with incremental steps of 1 µm. Micro ATR-FTIR analyses of the paint samples were performed by placing KBr cross-sectioned samples on the microscope stage and selecting the area of investigation through a 15× Thermo-Electron Infinity Reflachromat objective. Spectra were acquired in the range of 4000–650 cm^{-1}, at a spectral resolution of 4 cm^{-1}. A total of 64 scans were recorded and the resulting interferogram averaged. Data collection and post-run processing were carried out using a Nicolet Omnic-Atlus software. In this study, a micro-slide-on ATR silicon crystal (refractive index $n = 3.4$) directly connected to the objective has been used with opening of 80 µm × 80 µm, resulting in an investigated areas of about 25 µm × 25 µm. Single-point ATR analyses have been performed on samples MCR9, MCR12, MCR13, MCR13A and MCR22A. FTIR spectra of micro particles, collected directly from the paint cross-sections, have been performed in transmission mode by mean of a micro diamond cell or NaCl compression cell.

2.6 Gas chromatography—mass spectrometry

Paint samples were added with 10 µg of heptadecanoic acid (10 µl of a 1 mg/ml solution), 10 µg of norleucine (10 µl of a 1 mg/l solution) and 1 µg of norvaline (10 µl of a 0.1 mg/ml solution) each 1 mg of sample, as internal standards.

Fatty acid analytical procedure The material was treated with 4N–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). For the analysis of the fatty acid derivatives, the GC oven temperature program was: 80 °C for 2 minutes, then raised to 270 °C at 20 °C/min, followed by a 6 minutes isothermal period.

Amino acid analytical procedure After evaporation to dryness of the methanol phase, the residues were dissolved in 6N–HCl (2 ml) and hydrolysed in a screw-cap container for five hours at 100 °C in an oil bath, under nitrogen atmosphere. After evaporation to dryness, the hydrolysed 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 was dissolved in 2 ml of dichloromethane and derivatised with 0.2 ml of trifluoroacetic anhydride at 60 °C during one hour. After cooling, the solvent was evaporated under vacuum, and the residue was dissolved in 0.2 ml of dichloromethane; then the solution was used for gas chromatographic analysis (1 µl). For the analysis of the amino acid derivatives, the GC oven temperature program was: 60 °C for 3 min, 25 °C/min to 260 °C, and then isothermal for 6 min.

6890N GC system Gas Chromatograph (Agilent Technologies), coupled with a 5973 Mass Selective Detector (Agilent Technologies) single quadrupole mass spectrometer, equipped with split/splitless injector, was used. A VF-5 fused-silica capillary column (30 m × 0.25 mm × 1 µm) coated with a 0.25 µm film of methyl silicone (5 % phenyl) (FactorFour, Varian Inc., USA) was used for the separation. Helium carrier gas was set to flow 0.60 ml/min. The splitless injector was set to 280 °C with a 30 seconds purge off time. The MS transfer line was set to 280 °C. MS spectra were recorded in Total Ion Current (TIC, mass range 45–450).

3 Results and discussion

The characterisation of the painting constituents was obtained by analysing the cross-sections and the fragments, combining the results obtained by different techniques, as the real nature of a component is often difficult to assess with a single technique.

The optical microscope examination of paint cross-sections shows the presence of many layers, indicating the complexity of the paint stratigraphic morphologies. Therefore, the use of integrated analytical techniques was deemed necessary in attempt to clarify materials constitution and spatial location of both the inorganic and organic components, with the aim to obtain information about painting materials and to identify the original execution technique.

3.1 Stratigraphic analyses

Red paints In the samples MCR1 (Table 2) there is a first layer (layer 1) composed by cinnabar, red ochre and red lake and a thin *velatura* (layer 2) of red lake. These layers seem to represent the original polychromy. Concerning the overpainted layers, the first one is made of an orange red ochre and cinnabar paint layer (layer 3). Moreover, there is an irregular thin layer of gypsum, calcite and red ochre (layer 4), a layer of cinnabar and red ochre (layer 5). Two more overpainted areas seem to be present: layer 6 is made of red ochre, calcium carbonate and red lake, and layer 7 is composed by red ochre and gypsum.

In the sample MCR8 the results (Figs. 2 and 3) showed that in layer 0 gypsum, calcite, lead white, oxalates, oil (esters) are present; layer 1 is made of lead white, calcite, red lead, cerusite, gypsum, oxalates, oil (esters, acids, carboxylates), proteinaceous substances (amide I, amide II). The binding media has been identified as a mixture of oil (esters, acids, carboxylates) and proteinaceous substances (amide I, amide II). Probably layers 0, 1 and 2 are original; instead, the other five are overpainted layers. Layer 3 is composed of cinnabar, calcite, cerusite, oxalates, oil (esters, acids, carboxylates) and proteinaceous substances (amide I, amide II). Layer 4 is prepared with calcite, cerusite, oxalates, oil (esters) and proteinaceous substances (amide I, amide II). Moreover, there are two layers (layers 5 and 6) with lead white, red lake, cinnabar, calcite, red ochre, oxalates, oil (esters), proteinaceous substances (amide I, amide II). Layer 7 has been made with lead white, red lead, red lake, silicate, oxalates, oil (esters) and proteinaceous substances (amide I, amide II).

In the sample MCR12 (Figs. 4 and 5) above a brown layer (layer 0) a layer made of cinnabar, red lead, red lake and lead tin yellow is present (layer 1). Probably they are the original layers followed by overpainting: a brown layer (layer 2) and an orange layer (layer 3) composed of red lead, red lake, lead white and cinnabar and a second yellowish made of red lead, red ochre and lead white (layer 4). Cross-section observation under UV illumination shows the presence of two fluorescent yellow layers (layers 0 and 2). Micro ATR-FTIR analysis revealed the presence of siccative oil as the main component. The absence of a similar layer in samples MCR1 and MCR8 could be related to the deepness achieved in the sample collection procedure.

Table 2 Constitutive materials identified in the original layers

Colour	Sample	Paint layer	EDS	Integrated stratigraphic identification
Red	MCR1	2	Al, Si, Ca, K, Fe, Mg, Na	red lake, red ochre
		1	Hg, S, Si, Ca, Al, Fe, K, Na, Mg	cinnabar, red ochre, red lake
	MCR8	2	Al, Pb, S, Ca, Si, K, Na, Mg	red lake, gypsum, calcite, cerusite, oxalates, oil, proteinaceous substances
		1	Pb, S, Ca, Si, K, Na, Mg	white lead, calcite, red lead, cerusite, gypsum, oxalates, oil, proteinaceous substances
		0	Ca, S, Pb	gypsum, calcite, white lead, oxalates, oil
	MCR12	1	Pb, Hg, S, Al, Ca, Mg, Si, Sn	cinnabar, red lead, red lake, lead-tin yellow
		0		oil
Pink	MCR4	1	Pb, Ca, Si, S, Hg, Al, Na, Mg, Fe	white lead, cinnabar, red ochre
		0	Ca, S, Si, Al, Mg	gypsum, silicate
	MCR11	1	Pb, Si, Al, Fe, Ca, Hg, S, Mg	lead white, red ochre, cinnabar, calcium carbonate
		0		oil
	MCR20	2		lead white, red ochre, carbon black, green earth
		1		lead white, cinnabar, red ochre
		0		gypsum, silicates
Green	MCR9	2	Pb, Sn, Si, Ca, Al, Fe, K	red lead, white lead, lead-tin yellow, green earth, calcite, oil
		1	Pb, As, S, Si Ca, Al, Mg, Fe, K, P, Mn	orpiment, red lead, white lead, raw umber, calcite, oil
	MCR13A	2	Cu, Si, Pb, Cl, Ca, Fe	Cu pigments, yellow ochre, carbonate, oxalates, calcium carbonate, silicates, oil
		1	Cu, Ca, Fe, Si, Cl, Pb	Cu pigments, yellow ochre, hematite, carbonate, cerusite, oxalates, silicates, oil
		0		proteinaceous substances, oil
	MCR22A	2	Pb, Cu, Si, Ca, Al, Mg, K, Fe, Hg, S	lead white, malachite, cinnabar, red ochre, cerusite, silicates, calcium carbonate, oil
		1		gold
		0		organic compounds
Grey	MCR2	2	Pb, Si, Ca, P	lead white, calcium carbonate, bone black
		1	Pb	lead white
Gilding	MCR3	2	Au	gold leaf
		1	Pb, Si, Fe, S, Al, K, Ca, Mg, As, Hg, P	red lead, red ochre, cinnabar, orpiment, bone black, oil, resinous substances, oxalates, calcium carbonate, gypsum, lead carbonate
	MCR13	3	Au	gold leaf
		2		glue
		1	Pb	lead white, cerusite, oil

Pink paints Cross-section observations of MCR11 (Table 2) confirmed the presence of a discontinuous brown siccative oil layer under the first paint layer. Moreover, a whitish ground layer (layer 0) made of gypsum with the addition of few silicates is present in samples MCR4 (Fig. 6) and MCR20 (Table 2).

In the samples MCR4, MCR11 and MCR20 the flesh tonalities (layer 1 in samples MCR4, MCR11 and MCR20) were obtained by using lead white with few cinnabar particles and small amounts of red ochre and also of calcium carbonate in the sample MCR11. In addition, cross-section observation of sample MCR11 under UV illumination shows the presence of a thin pale-red fluorescent layer, which appears brown in the reflected light image, and it can be attributed to a red lake glazing intentionally applied by the artist in order to achieve the final original flesh tone. One overpainted layer made of lead white, red ochre, carbon black and green earth is present in both samples MCR4 and MCR20. In sample MCR11 three additional layers are present: two are made of lead white, cinnabar and calcium carbonate, while the third is a mixture of red lead, cinnabar, calcium carbonate, lead tin yellow and antimony yellow, and it represents the blood drop applied on the leg of S. Sebastian.

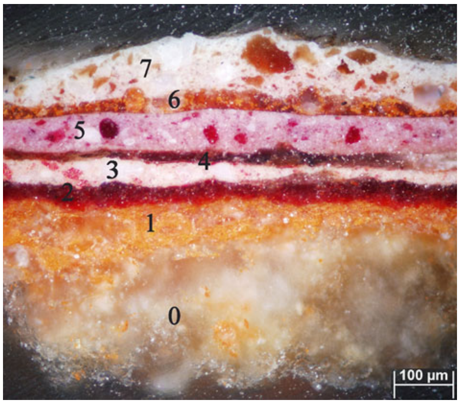

Fig. 2 Microphotografy of sample MCR8, visible light

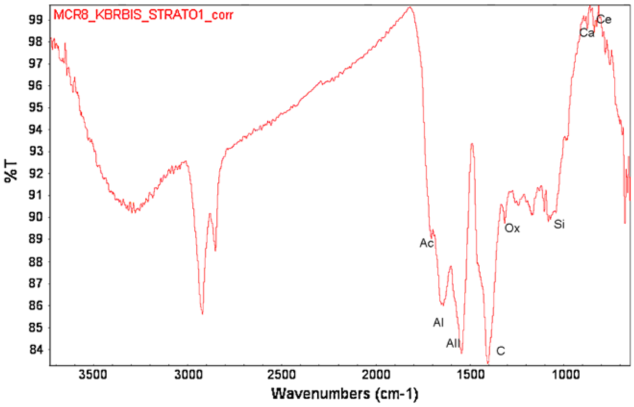

Fig. 3 ATR spectrum of sample MCR8 Ac = acid function; AI = Amide I; AII = Amide II; C = Carbonate; Ox = oxalates; Ca = calcium carbonate; Si = Silicates; Ce = Cerusite

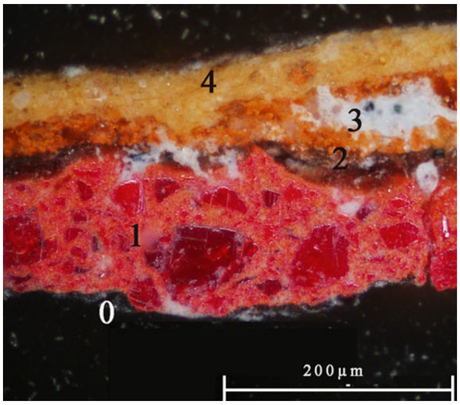

Fig. 4 Microphotografy of sample MCR12, visible light

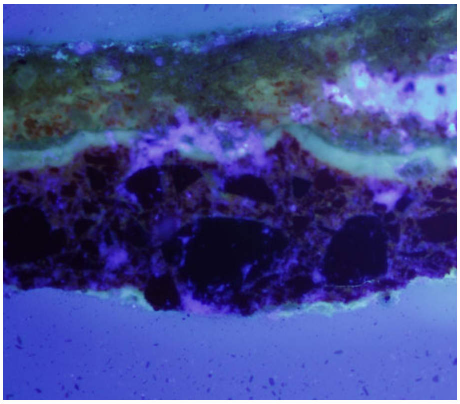

Fig. 5 Microphotografy of sample MCR12, UV light

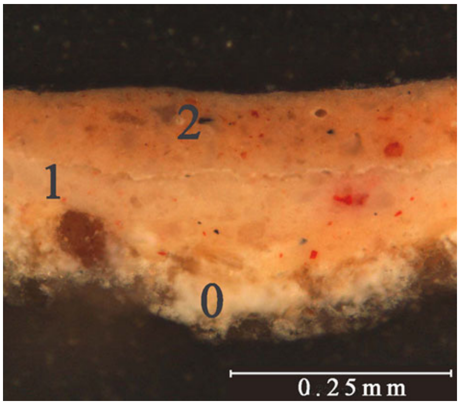

Fig. 6 Microphotografy of sample MCR4, visible light

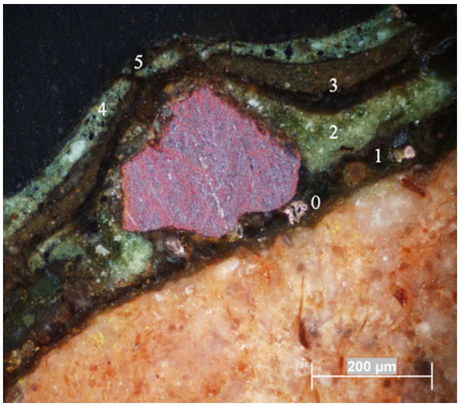

Fig. 7 Microphotografy of sample MCR13A, visible light

Green paints The green paint sample MCR13A presents a very interesting stratigraphy (Fig. 7). ATR-FTIR analyses showed the presence of proteinaceous substances and oil (layer 0) applied directly on the clay body.

FTIR microscopy analyses and SEM-EDS elemental mapping performed on the paint cross-section showed the presence of carbonate, cerusite, oxalates, silicates, oil, proteinaceous substances (layer 0). Cu based pigments, yellow ochre, hematite, carbonate, cerusite, oxalates, silicates, oil (esters, acid) in layer 1. Layers 2 is made of Cu based pigments, yellow ochre, carbonate, oxalates, calcium carbonate, silicates, oil (ester, carboxylates, acid); layer 3 is made of green earth, Cu based pigments, carbonate, oxalates, calcium carbonate, silicates, oil (esters, carboxylates). Layer 4

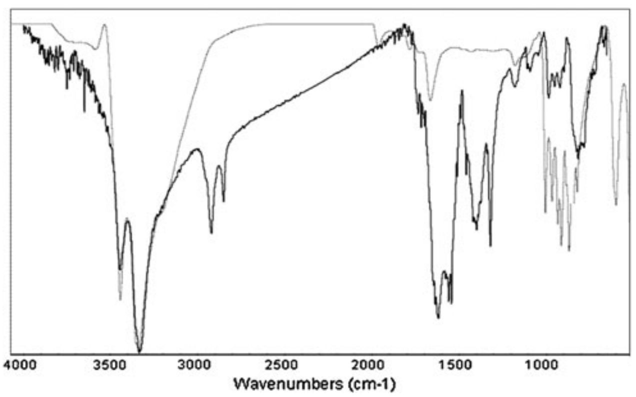

Fig. 8 Single point ATR spectrum (4000–650 cm^{-1}) of layer 5 of sample MCR9 (*continuous* line) and FTIR spectrum (4000–450 cm^{-1}) of a standard reference atacamite sample (*dotted line*)

is made of green earth, yellow ochre, Cu based pigments, carbonate, oxalates, calcium carbonate, silicates, lead white, oil (esters) proteinaceous substances (amide I, amide II). The last yellowish thin layer (layer 5) is made of calcium carbonate, red ochre and Cu pigments.

The sample MCR9 resulted to have a very complex stratigraphy, where only the layers 1 and 2 can be ascribable to the original paint. SEM-EDS elemental mapping performed on the paint cross-section shows that layer 1 is made with a mixture of orpiment, red lead, lead white, raw umber and calcite. The final green tonality has been achieved by glazing the underlying layer with a mixture of red lead, lead white, lead tin yellow, green earth and calcite (layer 2). Single point micro ATR-FTIR analyses performed stratigraphically indicated the contemporary presence of fatty esters and metal carboxylates, which are compatible with the use of siccative oil as binding medium [19].

Furthermore, SEM observation clearly identified a discontinuity visible in the BSE image. A dark thin layer accounts for the hypothesis over the upper pale yellow layer (layer 3) a copper resinate *velatura* (layer 4), was painted at a later stage. The other discontinuity observed in the BSE image demonstrates how the upper green paint layers (layers 5, 6 and 7) represent later overpaintings. SEM-EDS elemental mapping analyses and micro ATR-FTIR performed stratigraphically on layer 5 confirmed the presence of copper hydroxychloride, probably atacamite (Fig. 8) used as pigment, whereas the overpainting seems to have been painted with lead white, green earth with the addition of few calcium carbonate and bone black. The latter probably accounts for the blue tonality of the paint layer.

In the sample MCR22A (Table 2) the inner layer (layer 0) is made of organic compounds, probably applied as preparation of a gilding decoration (layer 1). The green layer 2 is constituted by lead white, malachite, cinnabar, red ochre, cerusite, silicates, calcium carbonate and oil (acids, carboxylates). In addition, over a gold leaf (layer 3), there are different overpainted layers. Layer 4 is made mostly of lead white, lead red, dolomite/calcite, oxalates, oil (esters, acids, carboxylates). Layer 5 is realized by the use of atacamite, azurite, malachite, oxalates and oil (acids, carboxylates), while the layer 6 is made of silicates, lead white, dolomite/calcium carbonate, gypsum, oxalates, oil (acids, carboxylates) and proteinaceous substances (amide I, amide II). The uppermost layer (layer 7) is made of green earth, red ochre, lead white, silicates, indigo, dolomite, oxalates, oil (esters, acids, carboxylates) and proteinaceous substances (amide I, amide II).

Grey paint Cross-section observation of sample MCR2 showed a morphological stratigraphy (Table 2) characterized by the presence of lead white (layer 1) on which a dark grey layer made of lead white, calcium carbonate and few bone black particles (layer 2) is applied. When observed under UV light illumination, the presence of a discontinuity between these layers and the upper pale grey paint (layer 3) made of lead white, calcium carbonate, red ochre and few big carbon black particles can be detected. This probably accounts for the possibility that the pale grey may represent a later paint application. Furthermore, the analytical results allow the identification of other two possible overpaintings aimed at achieving a yellowish tonality for the hairs. To paint the first layer (layer 4) a mixture of lead white, red ochre, smalt, lead-tin yellow and few azurite particles were used, whereas the lighter tonality of the second layer was achieved by the use of a mixture of lead white, calcium carbonate, yellow ochre and few carbon black particles.

Gilding Cross-section observation of sample MCR3 collected from a gilded area of the altarpiece lunette is characterized by the presence of just one layer (Table 2). The internal differentiation detectable within the paint layer when observed under UV light illumination can be related to the presence of a greater amount of red lake located in the external part of the paint layer which results to be constituted of a mixture of red lead, red ochre, cinnabar, orpiment and few bone black particles. Micro ATR-FTIR analysis shows the presence of resinous substances, oil, carboxylates, gypsum and oxalates. The large presence of red lead based paint is probably to be related to both the purpose of achieving a warm gilding tonality and increasing the drying time of the oil-binding medium. In fact red lead is most frequently historically mentioned among European sources in the context of driers (siccatives) added to oil.

The microscopic observations of blue sample MCR13 (Fig. 9) revealed the original gilding decoration of the angel wing. Over a first oil rich layer made of lead white (layer 1), a bolo pigment (layer 2) was applied and covered by proteinaceous material, with a gold leaf superimposed (layer 3).

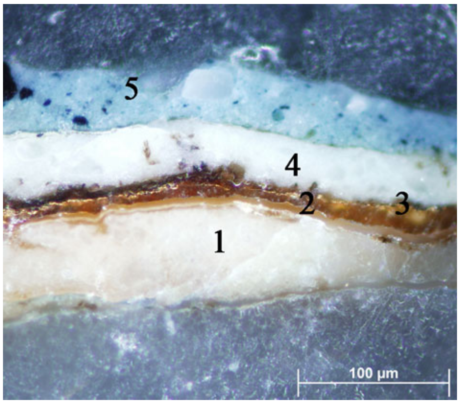

Fig. 9 Microphotografy of sample MCR13, visible light

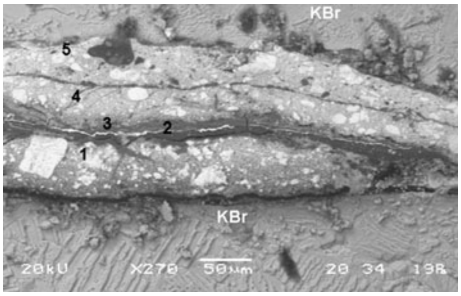

Fig. 10 Microphotografy of sample MCR13, BSE image

A dark thin discontinuity was identified by BSE observation (Fig. 10) over the gilding and it accounts for the hypothesis that two upper layers represent overpaintings. The first one (layer is made of a mixture of lead white and oil (layer 4) and a further blue paint made of lead white with oil as binder. Few particles of bone black and indigo have been identified by the NaCl compression cell micro-FTIR analysis of a single blue particle, directly collected from the layer 5 of the paint cross-section.

3.2 Lipidic and proteinaceous material characterization

Based on these first indications deeper information could be obtained with investigations carried out with analytical techniques that allow classifying the chemical nature of organic substances. Gas chromatography, coupled with mass spectrometry detector, was used to identify the lipidic and proteinaceous materials already observed in some samples by means of infrared micro spectroscopy analyses. The analytical method selected was based on a combined procedure for the characterisation of lipidic and proteinaceous materials on the same sample [20–22].

Two chromatograms were collected for each sample: the first one from fatty acid derivatives, the second from amino acid derivatives. The gas chromatograms of lipidic fraction of each sample are characterized by dicarboxylic acids, particularly azelaic acid, and saturated fatty acids, principally palmitic and stearic acids. In samples MCR1 and MCR2 miristic acid was also evidenced. In all the samples, the azelaic and palmitic acids ratio denote the presence of drying oil. The palmitic and stearic acids ratios allow classifying the kind of drying oil as linseed oil.

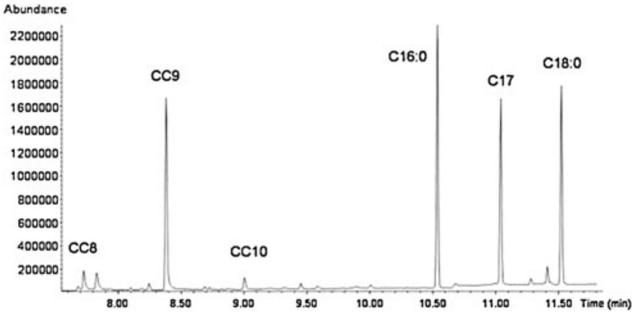

Fig. 11 Chromatographic profile of the lipidic fraction of MCR4 sample. CC8 = suberic acid, CC9 = azelaic acid, CC10 = sebacic acid, C16:0 = palmitic acid, C17 = eptadecanoic acid (I.S.), C18:0 = stearic acid

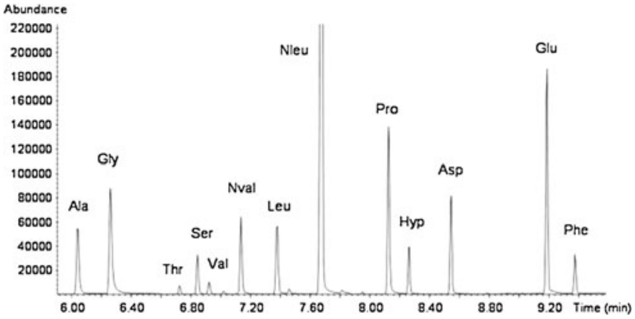

Fig. 12 Chromatographic profile of the proteinaceous fraction of MCR11 sample. Ala = alanine, Gly = glycine, Thr = threonine, Ser = serine, Val = valine, Nval = norvaline (I.S.), Leu = leucine, Nleu = norleucine (I.S.), Pro = proline, Hyp =hydroxyproline, Asp = aspartic acid, Glu = glutamic acid, Phe = phenylalanine

Figure 11 shows the chromatographic profile of the lipidic fraction of sample MCR4.

Furthermore in all samples the proteinaceous fraction characterized by the presence of amino acids was detected. In Fig. 12 the chromatographic profile of the proteinaceous fraction of sample MCR11 is showed. The characterization of proteinaceous material was made considering a set of eight amino acids: alanine (Ala), glycine (Gly), leucine (Leu), proline (Pro), hydroxyproline (Hyp), aspartic acid (Asp), glutamic acid (Glu) and phenilalanine (Phe). To distinguish between proteinaceous media, the amino acid content was subjected to multivariate data analysis according to the PCA (principal component analysis) method. The percentage areas of the eight amino acids previously reported, revealed in standard samples belonging to the reference collection of the *Opificio delle Pietre Dure* of Florence, were used as database [23, 24]. The loading plot (Fig. 13) highlights the important role that each amino acid plays in the

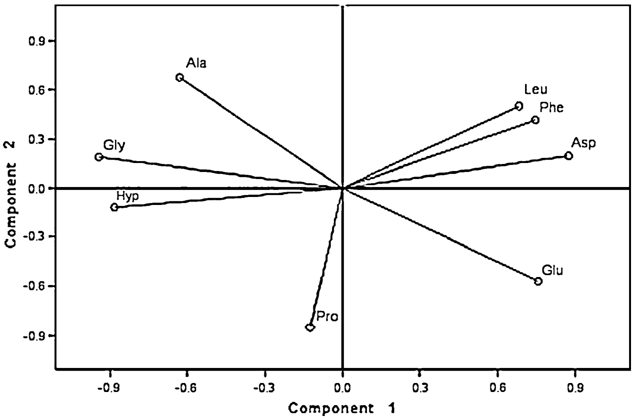

Fig. 13 Loading plot of the reference samples

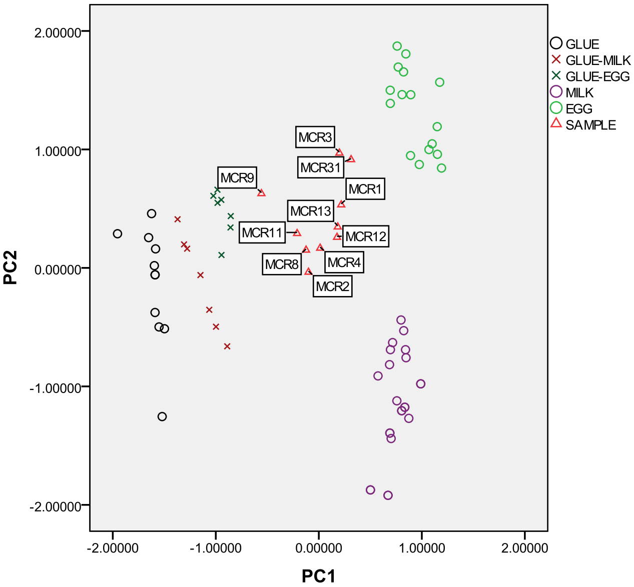

Fig. 14 Score plot of all samples

separation of clusters: alanine, glycine and hydroxyproline are responsible for glue cluster separation, while egg and milk parting is carried out by aspartic acid, leucine and phenilalanine versus glutamic acid and proline.

The evaluation by means of PCA, whose score plot is reported in Fig. 14, locates the samples a new cluster suggesting a mixture of animal glue and egg binder. The content of animal glue seems to increase for MCR2, MCR8, MCR9, and MCR11 shifted to negative values of PC1 corresponding to higher relative percentage values of glycine and especially hydroxyproline.

In Table 2 are reported the materials detected in the original layer achieved by means of the integrated use of different analytical techniques.

As the analytical results pointed out, proteinaceous material and siccative oil were found as constituents applied on the terracotta surface as *priming*. In two samples (MCR4 and MCR20), from the arms of the angels, a classic preparation with gypsum and glue is presents and it could be related to a smoothing treatment just on the rough arm surface or a former intervention of restoration.

From a general point of view, the scheme of polychromy found on terracotta statues is simpler than the one usually observed on paintings since the shape of the object is already achieved by its 3D structure and the colour does not need to be modulated. In spite of this, the original polychromy of Montecassiano altarpiece presents thin paint layers obtained with an extensive use of red lakes applied on the robe of the God (sample MCR1), on the mantel of *S. Rocco* (MCR12), on the leg of *S. Sebastian* (MCR11). Moreover, a green copper resinate was also found on the robe of the angel (MCR9). Two different gilding techniques were identified. In the case of the gilded wing of the angel (sample MCR13) the gold leaf has been applied over a glue mordant, whereas for the lunette (sample MCR3) a typical oil mordant composed of a mixture of red lead, red ochre, cinnabar, orpiment, bone black, calcium carbonate, gypsum, lead white, red lack, linseed oil, egg and resinous substances was used in accordance with ancient treatises [25, 26]. This oleo-resinous pigmented mixture is more frequent in wall paintings, but it was also founded in terracotta altarpiece [27, 28].

Finally, the present study reveals the presence of several overpainted layers related to restoration realized during the centuries that could ascribe to almost three different interventions. The absence of modern pigments suggests that they could be realised long ago.

4 Conclusion

The investigation carried out in this study allowed the characterisation of the original polychromy and painting technique adopted by Fra Mattia della Robbia to decorate the terracotta altarpiece, called *Coronation of Virgin between Saints Rocco, Sebastian, Peter martyr and Antonio abbot*, located in the collegiate church of S. Maria Assunta in Montecassiano (Macerata, Italy).

Optical microscope demonstrated the absence of a preparation in most of the samples.

Micro ATR-FTIR spectroscopy performed stratigraphically allowed us to identify proteinaceous and material under the first painted layer used as *priming*; furthermore, the contemporary presence of fatty esters and metal carboxylates in the original layers suggests the use of a siccative oil as binding medium.

The GC-MS analyses allowed identifying dicarboxylic acids, particularly azelaic acid and saturated fatty acids, principally palmitic and stearic acids; in one case miristic acid was also evidenced. The azelaic and palmitic acids ratio indicates the presence of drying oil. The palmitic and stearic acids ratio allowed classifying the kind of drying oil as linseed oil.

The proteinaceous materials detected by micro ATR-FTIR in overpainted layers were identified by GC-MS as egg and animal glue.

Integrated microscopies allowed us to identify the original pigments used: cinnabar, red lack, red lead, red ochre, hematite, Cu resinate, green earth, lead tin yellow, lead white, carbon black, bone black and gold. These pigments are also present in the overpainted layers with other pigments as antimony yellow, azurite, indigo, malachite and smalt.

Acknowledgements The authors wish to thank Dr. Gabriele Barucca of Soprintendenza ai Beni Artistici, Storici ed Etnoantropologici delle Marche, Urbino (Italy) in the collection of historical information.

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