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Multi-technique chemical characterisation of a 12–13th-century painted Crucifix

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ABSTRACT

The Crucifix panel painting in the Santa Maria a Mare church on the Isle of St. Nicholas (Isole Tremiti, Italy), painted on both sides, was executed between the late 12th century and the early 13th century and several times restored in the following centuries. The precious artefact was studied by various complementary analytical techniques in order to characterize the original medieval painting technique and the subsequently applied restoration materials. Optical microscopy (OM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), micro-Raman spectroscopy, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), and Matrix Assisted Laser Desorption Ionisation–Time of Flight–Mass Spectrometry (MALDI-TOF-MS) were applied on various samples taken from significant parts of the painting. The compositional data were used for a correct planning of the recent restoration treatments and as a support for the historical-artistic study of the painting. The results obtained confirm that both paintings—*recto* and *verso*—were realized by following the 13th century Italian painting tradition. Egg-based paint layers were applied on a gypsum/animal glue ground. Various pigments could be identified among which the precious lapis lazuli. Interestingly, the water-gilding of the *recto* was performed without the use of a bole layer. *Pinaceae* resin as well as acrylic resins were found.

1. Introduction

The Crucifix (see Fig. 1) in the *Santa Maria a Mare* church on the Isle of St. Nicholas (Isole Tremiti, Italy) is a rare example of a cross painted on both sides. A *Christus triumphans* is depicted on the *recto* together with mourning figures representations hosted onto two side panels. A nimbed *Agnus Dei* is present on the *verso* within a polychrome *clypeus* with phytomorphic and voluted decorations [1]. The Crucifix has been dated between the late 12th century and the early 13th century on the basis of stylistic comparison with contemporary paintings and icons [2].

In the past the precious Crucifix has been subjected to various restoration treatments some of which have been documented. In 1922 the Cross was "*liberata da ogni ciarpame e consolidata con opportuno restauro*" [freed from all lumbers and consolidated with an appropriate restoration]. At that time the cross was preserved within a gilded baroque case [3]. The inscription on the legs of the Christ—now illegible, but reported on the 17th century case—remembers of a miraculous journey of the Byzantine-Greek Crucifix from Greece to the Adriatic Isle.

Between the late 1950s and the beginning of the 1960s the painting has been thoroughly restored at the *Istituto Centrale del Restauro* (Rome, Italy) under the direction of Cesare Brandi. In several areas of the *recto* the painting showed detachments and the wood panel was severely damaged. Therefore, the ground and paint layers have been fully detached, transported on canvas and then re-applied on the restored original wood panel by interposing a layer of an unspecified "synthetic expanding resin". After some minute restoration treatments performed on site in the 1970–1980s, a new restoration program had to be undertaken due to the very bad conditions of the Cross (in particular, the intermediate layer of expanding resin of the recto appeared completely degraded). The planning of restoration treatments apt to solve the complex situation of the valuable Cross required an interdisciplinary approach, involving art historians, restorers, physicians, and chemists. In particular, various non-invasive imaging techniques (infrared, false color, ultraviolet, radiography) were employed and micro-destructive analyses were performed in order to obtain a complete characterisation of this important artefact. The data obtained during these preliminary investigations were useful for a careful set-up of the conservation treatments and could also support the historical-artistic investigation of the Crucifix. For the first time, a detailed material-technical comparison of both sides—*verso* and *recto*—of the painting could be performed.

This study reports on the chemical characterization of the Crucifix involving various complementary analytical techniques. Cross sections were studied by optical microscopy (OM) in visible, blue, and ultraviolet light, by micro-Raman spectroscopy, and by Scanning Electron Microscopy (SEM) in combination with Energy Dispersion Spectroscopy

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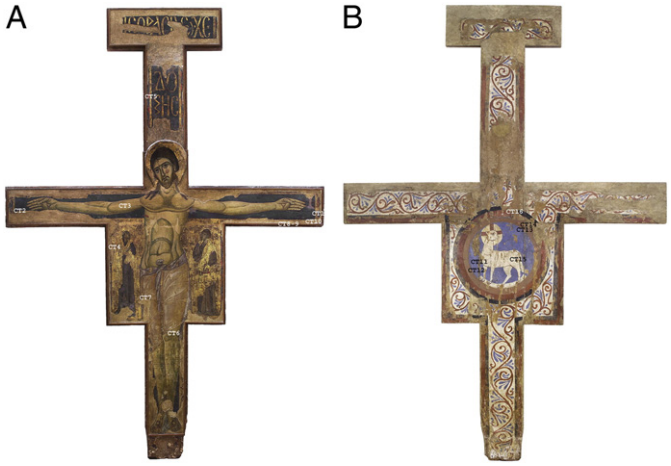

Fig. 1. Crucifix (cm 373, 5 h × cm 261 w) with indication of sampling points: (A) *recto*; (B) *verso*.

(EDS). The combined use of these techniques allowed to investigate the sequence, thickness, and composition of ground and paint layers. Identification of canvas fibers was performed by OM.

The organic materials were analyzed by Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) and Matrix Assisted Laser Desorption Ionization (MALDI)-Time of Flight (TOF)-Mass Spectrometry (MS).

Analysis of organic materials in artworks, i.e., paint binders, varnishes, consolidants, and adhesives, still challenges analytical techniques due to the complexity and low sample size; various methods such as GC/MS [4–7], Fourier Transform Infrared (FTIR) Spectroscopy [8,9], and micro-Raman Spectroscopy [10,11], have been proposed in the literature. Py-GC/MS is particularly suitable for the analysis of synthetic polymers [12–15] or polymeric fractions of natural resins [16–19], whereas MALDI-TOF-MS has recently been shown to be efficient in fast and complete identification of historic paint binders. In fact, since a decade the use of new mass spectrometric techniques based on soft ionization, such as MALDI [20–27] or Electrospray Ionization (ESI) [25–36] for investigation of organic materials as present in polychrome artefacts or archaeological finds has significantly increased. In particular, MALDI-MS offers a series of advantages such as direct analysis of complex mixtures with reduced sample pretreatment, short analysis times, relatively easy interpretation of results, and high sensitivity, fundamental in the study of paintings with very limited sample amounts. ESI-MS not only allows to identify proteins but also the protein species origin from few micrograms of artwork samples [31,33,35].

In this study, a previously described protocol [37,38] for MALDI-TOF-MS analysis of both the protein and lipid fractions of paint samples has been applied, allowing to obtain information on the presence of both classes of substances frequently used in mixtures or in subsequent layers [39]. In particular, the occurrence of egg and drying oil lipids degradation product markers could be evaluated, whereas proteomic approaches were applied to the protein fraction in order to integrate and/or confirm the information obtained from the lipid fraction analysis.

2. Experimental

2.1. Materials

α-Cyano-4-hydroxycinnamic acid (CHCA), 2,5-dihydroxybenzoic acid (DHB), ACTH 18–39 fragment, angiotensin I, renin, proteomic grade trypsin, dithiothreitol (DTT), iodoacetamide (IAA), Na_2CO_3, tetramethylammonium hydroxide (TMAH) (25% in H_2O) were obtained from Sigma-Aldrich (Sigma Aldrich, St. Louis, MO, USA). Lipids trilaurin (LLL), trimyristin (MMM), tripalmitin (PPP) and tristearin (SSS) from Supelco; RapiGest™ SF Protein Solubilization Reagent was from Waters (Bedford, MA). Water, acetonitrile (ACN), trifluoroacetic acid (TFA), methanol (MeOH), acetone, and chloroform ($CHCl_3$) (Sigma Aldrich) were HPLC grade and were used without further purification. Epoxy resin (Epokitt) for preparation of cross sections was purchased from Ilpa srl (Bari, Italy).

2.2. Samples, sample preparation and techniques

Seventeen samples were taken from the *recto* and from the *verso* of the Crucifix (sampling points are reported in Fig. 1 and in Table 1). Cross sections were prepared by embedding the fragments in epoxy resin, followed by cutting and polishing in order to allow transversal observation and analysis of the different layers. Specimens of cloth sample were prepared by boiling the threads in an

Table 1
Description of samples (reported in Fig. 1) and summarised results (numbers refer to the different layers by starting from the lowest layer).

	Description	Results
Recto		
CT-1	blue-black decoration	1) gypsum/animal glue ground, 2) carbon black and red ochre, 3) lapis lazuli and red ochre; egg
CT-2	blue background	1) gypsum/animal glue ground, 2) lapis lazuli, red ochre, carbon black, yellow ochre; egg; p(nBMA); oxidised *Pinaceae* resin
CT-3	flesh-colored arm	1) gypsum ground, 2) green earth, lead white, yellow ochre, carbon black, 3–4) yellow ochre, lead white, lapis lazuli, cinnabar
CT-4	gilding	1) *gesso grosso*, 2) *gesso sottile*, 3) *gesso sottile* rich in animal glue, 4) gold leaf
CT-5	red decoration	1) gypsum/animal glue ground, 2) cinnabar; egg
CT-6	flesh-colored leg	1) gypsum ground, 2) green earth, lead white, yellow ochre, carbon black, 3) yellow ochre, lead white, cinnabar, lapis lazuli
CT-7	loincloth	1) gypsum/animal glue ground, 2) yellow ochre, lead white, cinnabar, lapis lazuli, 3) lead white; egg
CT-8	I.C.R. finely woven canvas	cotton
CT-9	I.C.R. coarsely woven canvas	linen
CT-10	I.C.R. painted stucco	1) gypsum ground, 2) thin paint layer; p(nBMA)
Verso		
CT-11	*incamottatura*	linen
CT-12	blue background	1) gypsum/animal glue ground, 2) lapis lazuli, red ochre; egg; p(nBMA); p(MA-EMA); oxidized *Pinaceae* resin
CT-13	red-orange decoration	1) gypsum ground, 2) red ochre, 3) red lead; egg
CT-14	red decoration	1) gypsum ground, 2) red ochre; p(nBMA); p(MA-EMA)
CT-15	white lamb	gypsum
CT-16	black decoration	1) gypsum ground, 2) carbon black, red ochre; egg; p(nBMA); p(MA-EMA)
CT-17	I.C.R. expanding resin	toluene diisocyanate (TDI) polyurethane; polychloroprene adesive