Available online at www.sciencedirect.com
ScienceDirect
Journal of Cultural Heritage 9 (2008) 97–102
Journal of Cultural Heritage
http://france.elsevier.com/direct/CULHER/

Case study

Pigments and binders in ''Madonna col Bambino e S. Giovannino'' by Botticelli investigated by micro-Raman and GC/MS

Danilo Bersani [a,*], Pier Paolo Lottici [a], Antonella Casoli [b], Diego Cauzzi [c]

[a] *Dipartimento di Fisica, Università di Parma, Viale G.P. Usberti 7/a, 43100 Parma, Italy*
[b] *Dipartimento di Chimica Generale e Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Viale G.P. Usberti 17/a, 43100 Parma, Italy*
[c] *Soprintendenza per il Patrimonio Storico Artistico e Demoetnoantropologico, via Belle Arti, 56, 40126 Bologna, Italy*

Received 26 February 2007; accepted 25 May 2007

Abstract

During the restoration plan of the famous painting ''Madonna col Bambino e S. Giovannino'' by Sandro Botticelli, located in the Museo Civico of Piacenza (Italy), a study on painting materials was carried out. The pigments, the binders and the materials used for the application of ground and priming layers were studied using micro-Raman spectroscopy, gas chromatography coupled with mass spectrometry (GC/MS), optical and electronic microscopies. Gypsum and anhydrite were found in the ground layer, while carbon black and lead white were used in the priming layers. The precious pigments of the artist's palette and the binders used (egg and animal glue) were determined.

Keywords: Pigments; Binders; Micro-Raman; GC-MS; Botticelli; Paintings

1. Introduction

The painting ''Madonna col Bambino e S. Giovannino'', attributed to Sandro Botticelli and dated 1480–1485, has been conserved in the Musei Civici of Palazzo Farnese in Piacenza, Italy since 1903. It is the property of Piacenza municipality since 1862, when it was donated by the Oratory of the Bardi castle (Parma, Italy). The painting, executed on four poplar wood boards disposed horizontally, is round-shaped and formed like a *tondo*. The painting represents the Holy Virgin kneeling down, hands joined, looking at her Son. S. Giovannino wears a goat skin and a red cape and carries a cross made with canes. The scene is situated in a green field where one sees some cut roses, two plants of red roses in bloom and is back-grounded by a landscape. The frame is the original one, contemporary to the painting and attributed to Giuliano da Maiano.

The ''tondo'' was restored in 2004. Before the cleaning of the painting, micro-samples were taken in order to study the materials used by the painter. The study was focused on the pigments and organic binders media used by the artist in the paint layers and ground. The inorganic components of the priming layers and the ground were also studied to collect information on the painting technique. One of the aims of the study was to help clarifying if the whole picture had been carried out by Botticelli, or if some of it (in particular the figure of S. Giovannino) should be attributed to a different hand.

2. Experimental methods

A very small amount of painted materials (four samples, each the size of a few mm^2) were taken from damaged areas near the frame of the painting (Fig. 1), without damaging the picture further. All the paint layers of each sample, from the surface to the ground layer are present. One sample was taken from the original wooden frame to identify the binding media under the gilded layer. The sampling was carried out at the beginning of the restoration work. For a more detailed

* Corresponding author. Tel.: +39 0521 905 278; fax: +39 0521 905 223.
E-mail address: bersani@fis.unipr.it (D. Bersani).

1296-2074/$ - see front matter © 2007 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.culher.2007.05.005

Fig. 1. The Botticelli's *tondo* and the sampling points.

study of the paint materials, especially those present in the paint layers below the surface, cross sections were prepared by embedding fragments of the samples in epoxy resin. The untreated samples and the cross-sections were observed and photographed with an optical microscope.

The main technique used to determine the pigments used by Botticelli was the micro-Raman spectroscopy which allows the identification of organic and inorganic substances without any preparation of the sample [1–3]. The Raman micro-spectroscopy apparatus is a Jobin-Yvon Horiba Labram, equipped with a micrometric xy motorized stage and a He–Ne laser (632.8 nm) as excitation. The spectral resolution is about 2 cm^{-1}, while the spatial resolution is of the order of 2 μm.

The determination of the organic binding media was carried out by means of gas chromatography/mass spectrometry (GC/MS) which is very sensitive and specific in determining organic substances. The analytical method used was based on a combined procedure for the characterisation of drying oils [4] and proteinaceous materials [5,6] on the same sample.

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 g/l solution), and 1 μg of norvaline (10 μl of a 0.1 mg/ml solution) per 1mg of sample, as internal standards.

2.1. 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 was 80 °C for 2 min, then it was increased to 270 °C at 20 °C/min, followed by a 6 min isothermal period.

2.2. Amino acid analytical procedure

After evaporation to dryness of the methanol phase, the residues were dissolved in 6N hydrochloric acid (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 2 N HCl in propan-2-ol at 90 °C for one our. After cooling, the solvent was evaporated under vacuum and the residue of the paint was dissolved in 0.2 ml of dichloromethane and derivatised with 0.2 ml of trifluoroacetic anhydride at 60 °C for an 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). 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; then isothermal for 6 min.

The 6890N GC system gas chromatograph (Agilent Technologies), coupled with a 5973 Mass Selective Detector (Agilent Technologies) single quadrupole mass spectrometer equipped with PTV injector was used. A VF-5 fused-silica capillary column coated with a 0.25 μm film of methyl silicone (5% phenyl), FactorFour, Varian Inc. (USA) was used for the separation (30 m × 0.25 mm × 1 μm). Helium carrier gas was set to flow 0.60 ml/min. The splitless injector was set to 280 °C with a 30 s 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).

In addition, SEM-EDS Philips SEM 505 measurements have been carried out on a couple of samples in order to detect the elements present.

3. Results and discussion

3.1. Sample 1

The sample was taken from a green region of a leaf painted near the right bottom rim.

The cross-section shows four different layers (Fig. 2a): a white ground layer underneath, a black thin priming layer, a green paint layer containing blue and green grains and smaller yellow grains, and the outer varnish layer.

The Raman analysis performed on the white ground layer shows the presence of anhydrite (anhydrous calcium sulfate – $CaSO_4$) [7], which was often used together with calcium sulphate dehydrate (gypsum) in the preparation of the ground layers in paintings on wood. The priming black layer was carried out by using amorphous carbon (carbon black).

The micro-Raman spectra performed on the paint layer show that the blue grains are composed of lazurite $(Na,Ca)_8(AlSiO_4)_6(O,S,SO_4)_{1-2}$ which is the main component of lapislazuli [7,8], while the green grains are malachite $CuCO_3 \bullet Cu(OH)_2$ [9] (Fig. 3), a very common green pigment. The shape and colour of the grains suggest that synthetic malachite was used. Some green grains appearing on the outer surface of the untreated sample show the Raman spectra of