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Mineralogical, petrographic and chemical analyses for the study of the canvas "Cristo alla Colonna" from Cosenza, Italy: a case study

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Abstract - A multi-technique study on materials used for the painting "*Cristo alla Colonna*" by Luigi Bria (private collection, Cosenza, Italy) was carried out for the first time during the restoration plan. Pigments, binder media and raw materials used for the application of ground and priming layers were studied using optical (OM) and electronic microscopy equipped with energy dispersive spectroscopy qualitative microanalysis (SEM-EDS), infrared spectroscopy (FTIR) and gas chromatography coupled with mass spectrometry (GC/MS). The goal of this study was to characterize this canvas and to set up a scientific aid and guide for its restoration, taking into account the, severe damage not exclusively due to natural decay processes. Our data can provide information about historical and stylistic background as well as advises for correct planning of the cleaning procedures.

Riassunto - Il dipinto su tela "Cristo alla Colonna", opera di Luigi Bria (collezione privata, Cosenza, Italia), è stato sottoposto, durante le fasi di restauro, per la prima volta ad indagine strumentale tramite varie tecniche analitiche. I pigmenti, i leganti ed altri materiali utilizzati per la sua realizzazione sono stati analizzati tramite microscopia ottica (OM), microscopia elettronica e microanalisi tramite spettrometria a dispersione di energia (SEM-EDS), spettroscopia infrarossa (FTIR) e gascromatografia accoppiata spettrometria di massa (CG/MS). Lo scopo del lavoro è stato quello di offrire una caratterizzazione dell'opera pittorica, nonché fornire un supporto scientifico ad un un corretto intervento di restauro su un'opera fortemente degradata. I risultati hanno permesso di fornire informazioni di natura storico-artistico nonché informazioni utili ad un corretto intervento di pulitura della tela oggetto di questo studio.

Key words: *Italian canvas; multi-technique approach; restoration.*

Introduction

Physical, chemical and structural investigations of paintings, essential components of worldwide cultural heritage, represent essential tools for their characterization. The resulting scientific information are basic for highlighting the various stages of the degradation processes as well. They can be also useful to suggest appropriate restoration procedures and to plan conservation projects (Mora *et al*.,1984; Botticelli, 1993; Henderson, 2000; Ciliberto and Spoto, 2000; Matteini and Moles, 2002a; Matteini and Moles, 2002b). For the first time multi-technique investigations were

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carried out on small fragments sampled in the painted on the canvas named "*Cristo alla Colonna*" (Fig. 1), preserved in the private collection located in Cosenza (southern Italy). The author, probably Neapolitan seems to be "Luigi Bria" and the date reported on the painting is "8 September 1849, Naples". "Cristo alla Colonna" canvas, shows the figure of Jesus with crossed hands and only thong tied to the right side. Rope, that usually accompanies such type of iconography, is not present. Alongside the scarlet cloak lying on the ground, there are Christian symbols of the Passion (whip and cane).

This painting has never studied before; it can be considered an important artwork because Luigi Bria represent an important artist, studied by critics despite at the state of art they are only fragmentary information on him. (Spinosa, 1997)

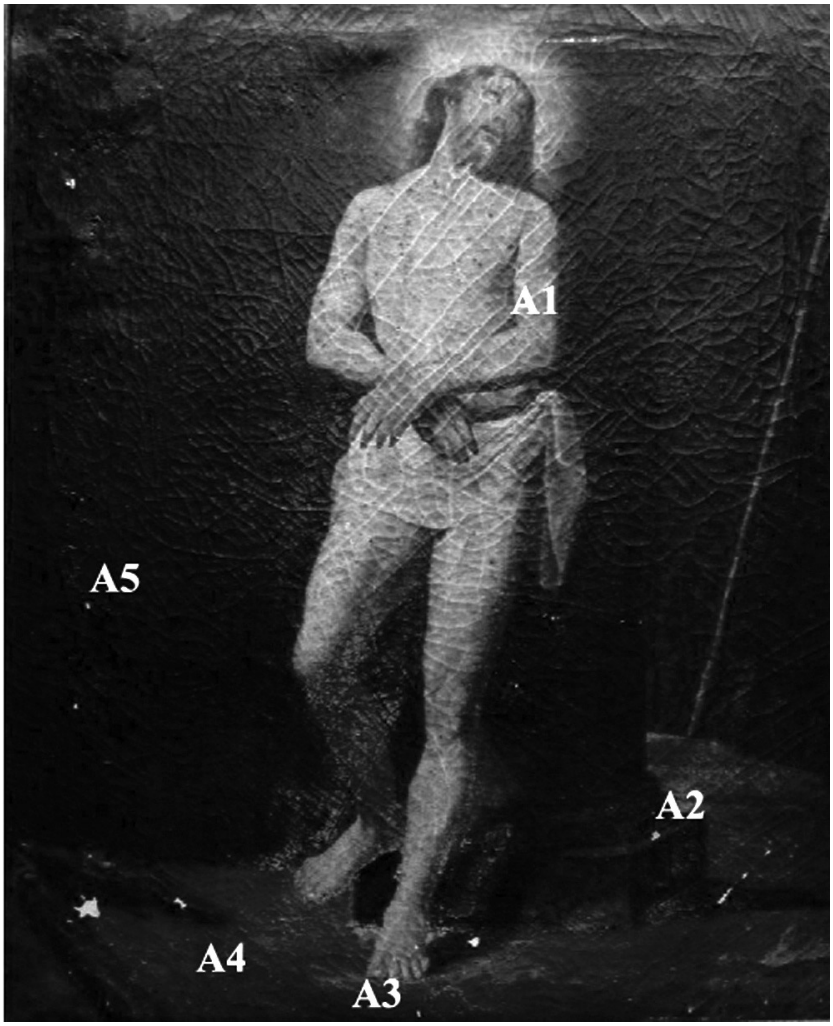

Fig. 1 - The canvas painting "Cristo alla Colonna" (45x63 cm); the sample points are also reported.

We have undertaken a characterization study of some representative samples coming from various zones of the painting by combined mineralogical, petrographic, chemical and spectroscopic techniques, in order to obtain useful information about the painting technique, to ascertain the type and the extent of the degradation processes which affected the canvas and to detect the materials used in previous restoration attempts. Moreover, this research would offer a guide for an adequate restoration project of this artefact; the canvas showed an advanced state of deterioration that has made it necessary a marked recovery intervention. At an first visual inspection the canvas appeared to be damaged in both the protective film, which was uneven and oxidized, and in the pictorial layer, that was characterized by exfoliation, fragmentation, vacancies and by the typical craquelure structure.

Sample description and methods

Five samples, mostly smaller than 5 mm, were collected from different scenes and decorative elements (Table 1 and Fig. 2). Sampling was conducted following the restoration procedures of and according to a principle of minimum invasiveness, i.e. taking samples from the margins of existing lacunae.

Preliminary study has consisted in optical microscopy (OM) observations of the samples, prepared on purpose as cross-sections, by means of a Zeiss Axiolab polarizing microscope equipped with transmitted/reflected light apparatus. This technique has allowed us to recognize the painting techniques and the textural relationships between the various microstratigraphical units across the painting sections. A first identification of the binder types and their microstructural features has been made as well. Morphological observation and elemental characterization of samples were performed using a FEI Quanta 200F (Philips) scanning electronic microscope (SEM), coupled with an energy dispersive X-ray spectrometer (EDS). All the SEM-EDS analyses were carried out with an acceleration voltage of 20 kV and under low vacuum conditions (10^{-5} mbar pressure). A Fourier transform infrared spectrometer (FTIR, Perkin–Elmer Spectrum 100 instrument) has been used to obtain molecular information on binders. IR spectra were recorded on powder pellets in ATR mode in the range of 4000-650 cm^{-1}, with a resolution of 4 cm^{-1}. Organic binder media have been analysed by gas chromatographic analyses coupled with mass spectrometry (GC/MS), due to its high sensitivity in determining the nature of organic substances (e.g. drying oils and proteinaceous materials). A gas chromatograph (6890N) coupled with a 5973 mass selective detector (both from Agilent Technologies) and a single-quadruple mass spectrometer was employed.

Results and discussion

OM, SEM-EDS

Under the optical microscopy and on reflected light, all samples show different stratigraphic typologies.

Sample A1 is constituted by a flesh coloured painted layer. Elemental analysis reveals an high lead content due to the presence of white lead, likely composed of hydrocerussite

$[2PbCO_3 \cdot Pb(OH)_2]$ (Fig. 3a)

This pigment is synthetic and used up to the nineteenth century; afterwards, because of its high toxicity, it was replaced by zinc white and in the twentieth century by "*titanium white"* (Matteini and Moles, 2002a). EDS microanalyses have also revealed the presence of antimony (Sb) and iron (Fe) in small amounts, probably related to the yellow pigment called "*Naples Yellow"* which is mainly formed by lead antimonate $[Pb_3(SbO_4)_2]$. Furthermore, the presence of traces of sulphur (S) and mercury (Hg) in the spectrum can be related to the presence of cinnabar (HgS), a well known red pigment. All these chemical component are coherent with the formulation of

the flesh colouring , normally made of a mixture of white, with small amounts of yellow and red.

Sample A2 consists of a white priming covered by a green pigmented layer. EDS spectra show lead in the white preparation, whereas in the green layer several elements have been detected, i.e. Fe, Si, Al, K, Ca together with Pb (Fig. 3b). Both morphological observations showed a clay platelet mineral (Fig. 4a) and EDS qualitative microanalysis can indicate the presence of clay minerals, the so-called "*green earth"* (Matteini and Moles, 2002a).

Specimen A3 is composed of two layers, as shown by image analysis obtained from backscattered scanning electron microscopy (BSE-SEM) given in Fig. 4b. Qualitative EDS analysis has highlighted the presence of different pigments (Fig. 3c). Lead was used for the white

Table 1
List and description of samples.

Sample	Description
A1	Christ's left bicep. Flesh colour
A2	Base of the column, where Christ is rested. Green
A3	Base under left foot. Dark brown
A4	Base, left side of the painting. Dark brown
A5	Background, left side of painting. Black

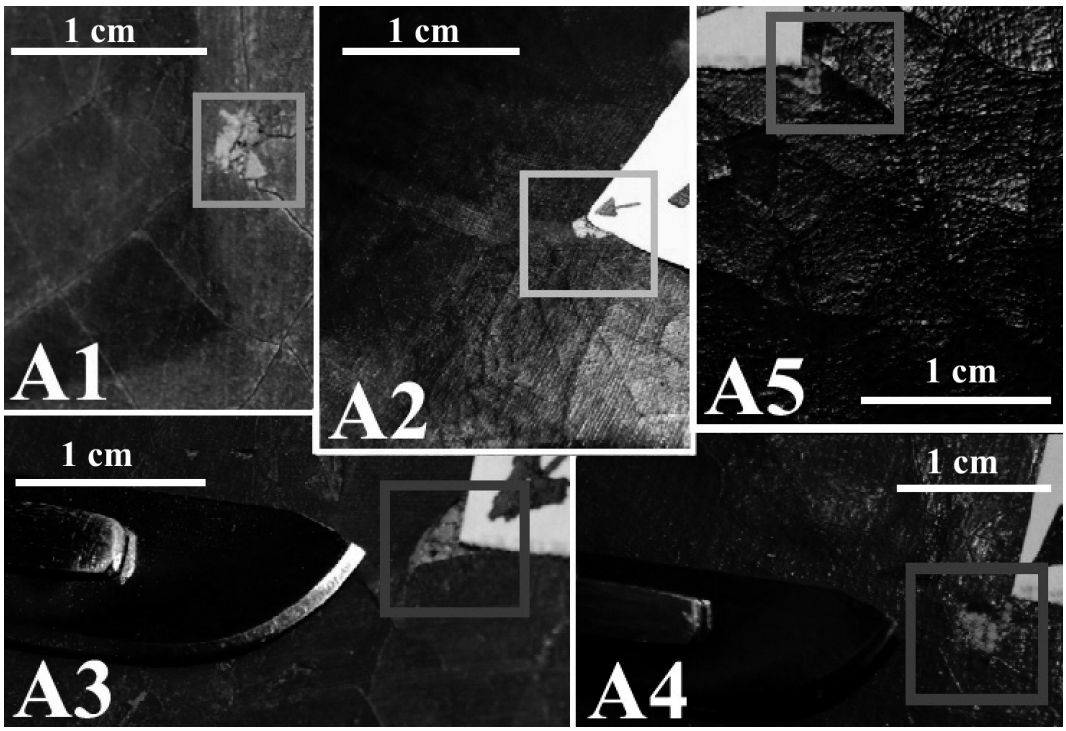

Fig. 2 - Details of sampling points shown in Fig. 1.

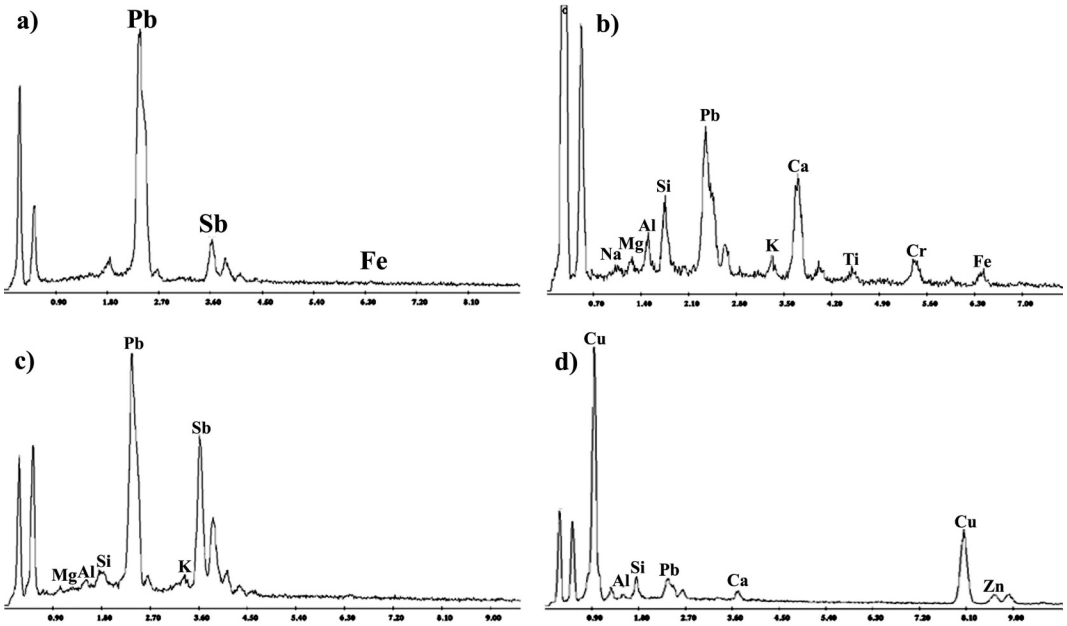

Fig. 3 - Selected EDS spectra of: a) sample A1, b) painted layer in sample A2; c) selected area in painted layer in sample A3; d) selected area in painted layer in sample A3.

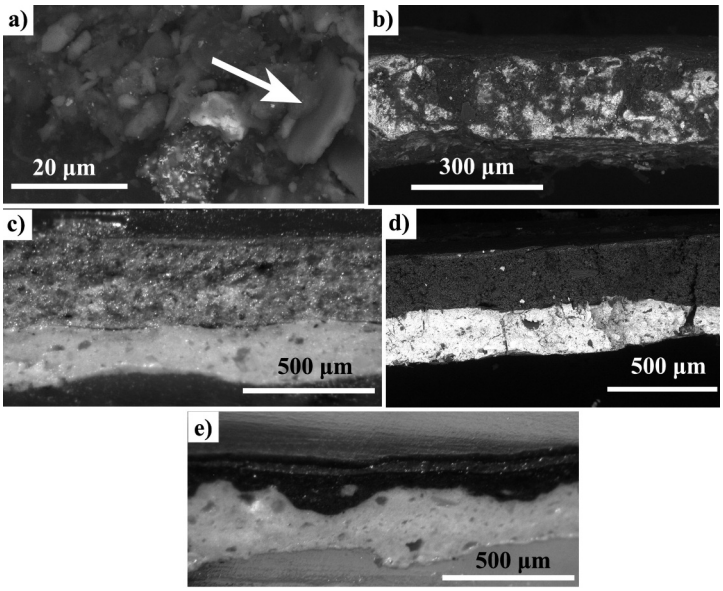

Fig. 4 - a) BSE-SEM image of a detail of painted layer in A2 sample, the arrow indicates a clay mineral habitus; b, d) BSE-SEM micrographs of samples A3 and A4; c, e) Cross section images acquired by optical microscope, visible reflected light mode, of sample A4 and A5.

preparation. In painted layer, elemental analysis (Si, Fe, Mg, K) and chromatic evaluation are coherent with the presence of "*green earth*" and other clay minerals, "*verderame"*

$$[Cu(CH_3COO)_2 \cdot 2Cu(OH)_2]$$

or malachite

$$[CuCO_3 \cdot Cu(OH)_2]$$

The occurrence of the latter two mineral components can be suggested by the presence of copper in the EDS spectrum (Fig. 3d). A copper acetate was probably used for brighten up the green pigments (Matteini and Moles, 2002a). The presence of Sb can be due to the Naples Yellow pigment (Fig 3c).

Cross-section and BSE-SEM micrographs of sample A4 has pointed out three different layers (Fig. 4c, d): a white ground with a maximum thickness of about 450 μm; a brownish painted layer and a translucent reddish thick layer (40 μm). Micro analytical data indicate the presence of lead in the white preparation and calcium sulphate on the upper surface of the sample, coming probably from a previous restoration attempts.

Sample A5 shows four different layers (Fig. 4e), e.g. an homogeneous superficial layer brown in colour, a layer with a lighter colour, a third layer constituted by a mixture of a dark groundmass and grains with different size and shape. Finally it is visible a preparation layer. Microanalytical data show similar composition to A4 sample.

FTIR spectroscopy

FTIR investigations, carried out on different painting layers, gave further information on the original binding materials and on inorganic and organic materials which form the samples. All spectra collected show typical features lipidic matter. A representative FTIR spectrum (sample A4) is reported in Fig. 5. It is evident a carboxylic ester (attributable to oils) due to the band at 1764 cm^{-1} (C=O) and the peak centred at 1163 cm^{-1} assigned to stretching of C-O-C (Favaro *et al*., in press). Bands at 1463 cm^{-1} represent the bending of CH_2 groups. Furthermore spectra revealed various abundances of calcium oxalate

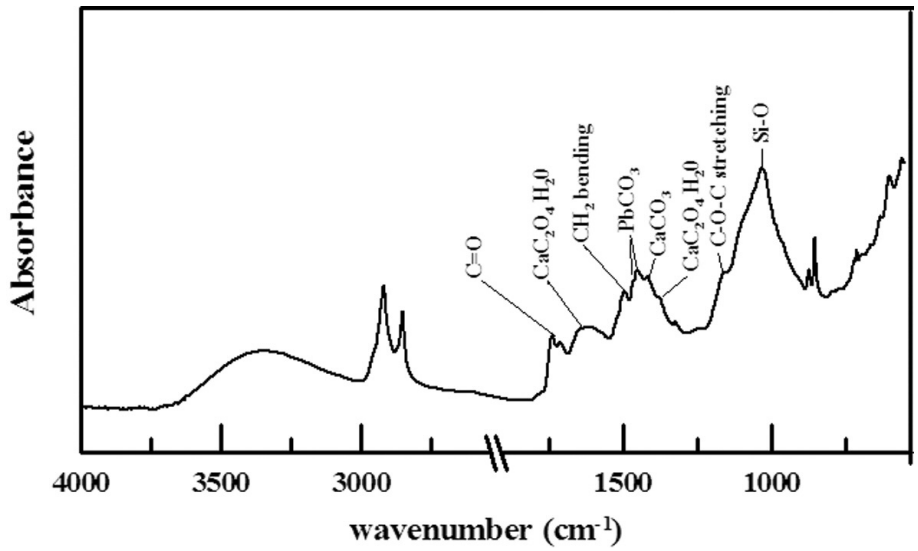

Fig. 5 - FTIR spectrum of sample A5.

monohydrate ($CaC_2O_4 \cdot H_2O$), commonly called whewellite, highlighted by bands at 1640, 1324, 786 and 680 cm^{-1} (Rampazzi *et al.* 2004). Calcium carbonate ($CaCO_3$) vibrations are peaked at 1409, 705 and 611 cm^{-1}, while silicates were identified by signal at 1032 cm^{-1}. Finally in samples A3, A4 and A5 it is evident the lead carbonate bands centred at 1438 e 1419 cm^{-1} (Cotte *et al*., 2007).

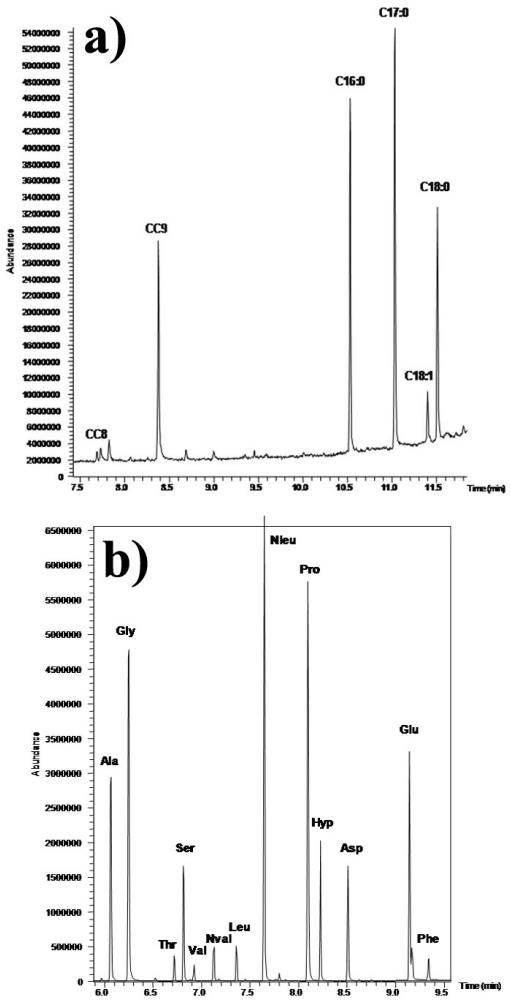

Fig. 6 - a) CG chromatogram of lipidic and b) proteinaceous fractions extracted from sample A5.

GC/MS analysis

Painted layer of sample A5 were analysed by GC-MS technique as well, because it ca give additional information on organic compounds of binder media. Chromatogram of the lipidic fraction shows the presence of dicarboxylic acids (CC8 - suberic acid, CC9 - azelaic acid) and monocarboxylic acids both saturated (C16:0 - palmitic acid, C18:0 - stearic acid) and unsaturated (C18:1 - oleic acid) (Fig. 6a).

The presence and the amount of azelaic acid, whose formation is due to the oxidation of unsaturated acids, and oleic acid suggests that the observed lipidic fraction can be attributed to siccative oil. Concentration ratios between azelaic /palmitic acid (0.82) and palmitic /stearic acid (1.33) revealed the presence of linseed oil. (Casoli *et al.,* 1999).

GC/MS data have demostrated the presence of proteinaceous matter, not been revealed by FTIR analysis. Chromatogram of amino acids is shown in Fig. 6b. To identify its real nature, the amount of 8 amino acids were considered (alanine, glycine, leucine, proline, hydroxyproline, aspartic acid, glutamic acid, phenylalanine). A comparison between results and a suitable set of reference proteinaceous material has been conducted according to the multivariate statistical analysis by means of principal component analysis method (PCA), which provides a rapid classification of unknown samples (Casoli *et al*.,1995, 1996, 2001). Main components are a linear combinations of original variables (the 8 amino acids considered). The use of PCA, whose result is shown in Fig. 7, classifies the sample in the animal glue group.

Conclusions

Multianalytical strategy allowed us to fully characterize both inorganic and organic components of the painting materials used in "Cristo alla Colonna". The painting technique

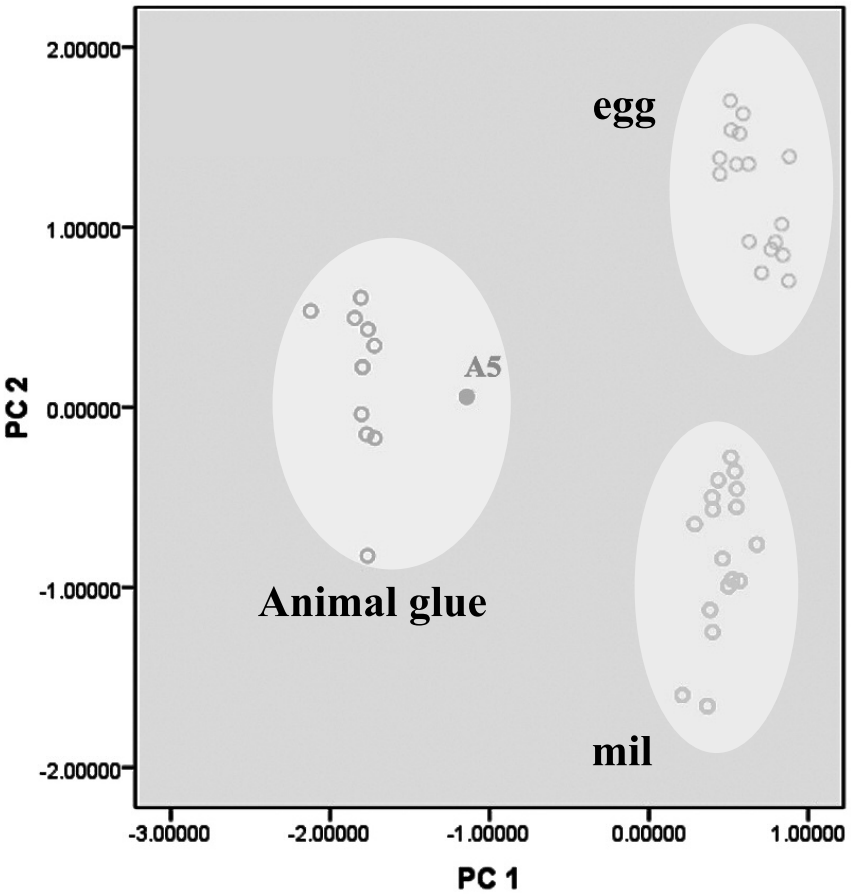

Fig. 7 - PCA chart. Classification of reference samples (animal glue, egg and milk) and sample A5 on the basis of their amino acidic composition.

emerging from mineralogical, petrographic and chemical data is consistent with the period in which it was framed, i.e. mid-nineteenth century. In particular GC/MS analyses suggest the presence of animal glue and linseed oil as binders. This latter result could to be useful for suggesting the conservation procedures, especially for the cleaning method to be adopted. A proper cleaning action allowed to recover iconographic details that were completely obliterated by alteration of the painting surface.

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