

MATERIALS AND PAINT TECHNIQUE OF A SPECIAL MASTERPIECE: JACOPO TINTORETTO'S *THE WEDDING FEAST AT CANA IN VENICE*

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Abstract

*The present paper illustrates the results of the scientific investigation performed on the painting on canvas *The Wedding Feast at Cana* (1561) by Jacopo Robusti, nicknamed Tintoretto. The painting, commissioned for the refectory of the Crociferi's Convent of, is located in the Sacristy of the Basilica della Madonna della Salute in Venice, after the dissolution of the congregation. Noninvasive single spot technique (X-ray fluorescence), and analytical investigations (optical microscopy, scanning electron microscopy with energy dispersive spectroscopy, and gas chromatography coupled with mass spectrometry) on ten micro-samples were combined to retrieve the palette and identifying the organic binding media. The investigations revealed the existence of many pigments available at that time in Venice, among which is the precious lapis lazuli. The identification of two pigments, one white and one blue, allowed to know the possible time of execution of the two angles, added at the top. The study of the painting has made it possible to know completely unexpected aspects: the painting does not present the traditional ground of gypsum and animal glue, but it turns out to be complete without the preparatory layer. This painting is described by art historians as an "oil on canvas"; however, GC/MS did not identify any fatty acids of siccative oil, but only egg, presumably yolk, then *The Wedding Feast at Cana* was made in tempera.*

Keywords: *Non-invasive analyses; Tempera on canvas; Organic binders; Pigments; Tintoretto; The Wedding Feast at Cana*

Introduction

From a scientific point of view, Jacopo Tintoretto is one of the most studied artists. The reason lies not only in the importance of this extraordinary Venetian painter, but also and above all in his *modus operandi*. Since the first studies of the middle of the nineteen seventies, emerges the portrait of a very eclectic artist, able not only to perform imposing works in a very short time, but also to work by kneading different materials, sometimes not compatible with each other, depending on the desired pictorial effect [1, 2].

The first in-depth results deal with some paintings from the National Gallery in London, in particular *S. George and the dragon*, *Christ washing his disciples' feet*, *The origin of milk way*, *Portrait of Vincenzo Morosini* [3-6], as well as various masterpieces preserved in Venice, in particular in the Banco del Sacramento of the parish church of S. Margherita [7], in the Church of San Simeon Grande [7], in the Church of Madonna dell'Orto, [8] and in the School of San Rocco [9-11].

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The numerous analytical campaigns have focused mainly on colour, since this is often irreparably altered, it has been observed that some authors have proposed virtual restorations in which to reinterpret the works hypothesizing, in a choice sometimes questionable, those that were to be the original colours [12].

In the course of the restoration of the canvas *The Wedding Feast at Cana* (435×545cm), preserved in the *Basilica della Salute*'s Sacristy, it was considered important to integrate the accurate studies of the historical-artistic character of the work, with an analytical campaign aimed at the knowledge of pictorial materials and the way they were put into work by the artist. It is wanted, that is, to investigate thoroughly not only on the palette of the artist and on the way in which the colors have changed in the visible part of the work, but also and, above all, on the most hidden and hardest to study. It refers to the characterization of the binding media of the color, to the study of the structure of the pictorial films, that is to say the measurement of the thickness and the number of the brush strokes, the presence of inner layers, "pentimenti", interruptions of work and any other details that can provide information about the painter's technological choices and operating modalities in performing the painting.

Two angles were added to the painting in the upper part, to give the rectangular shape to the work, during past interventions of restoration.

The diagnostic project was based, first of all, to the utmost respect for the work. For this reason, the chosen path initially envisaged the execution of a series of chemical investigations by X-ray fluorescence (XRF), with the aid of a portable non-invasive instrumentation [13]. Through the XRF it has been possible to recognize, quickly and without physical contact with the painting, most of the inorganic pigments present in the color, identifying the chemical elements. Finally, after processing the data that emerged on thirteen measuring points, ten micro samples of paint material were taken in a targeted way in order to acquire the information otherwise not obtainable with non-invasive techniques, or to complete the data available.

Micro sample analyses are currently indispensable for at least two reasons. The non-invasive diagnosis is not, in fact, able to identify all the components of the color, in particular organic materials, namely binders, some organic pigments, such as lacquers.

Without drawing a micro fragment of color and observing it under a microscope it is not even possible to have a precise idea of how the different components are distributed and therefore to have indications about the executive technique of a painting, from the preparation to the repainting and varnishing. For these reasons, the research has been deepened through the preparation and the study of stratigraphic sections of the paint material [14].

Analyses aimed at the identification of organic binders were done first with micro chemical tests and, subsequently, gas chromatography coupled to mass spectrometry (GC/MS) has been used. This technique allows the characterization of the organic matrix, by determining the content of fatty acids resulting from the lipid material, and amino acids derived from protein material.

Experimental

Samples

Based on preliminary non-invasive investigation, a total of 5 micro-samples (samples A, B, C, D, and E) were collected from the painting, by detaching a small portion of material to prepare the cross-sections. Sample A was taken in the corner part added. The cross-sections have been realized, according to an analytical methodology now consolidated [14], and in accordance with the current regulations regarding the diagnostics for the cultural heritage, by incorporating in cold-cured polyester resin the micro fragments of the paint material that, at a first observation to the stereo-microscope, appeared more significant. Another 5 micro samples were taken, in different chromatic points for the analysis of the organic binding media (samples F, G, H, I, and L). Figure 1 shows the points where the samples were taken.



Fig. 1. The painting on canvas *The Wedding Feast at Cana* by Jacopo Tintoretto: the numbers indicate the points where the samples were taken

Instruments and methods

Optical Microscopy (OM)

An optical microscope Nikon TK-1270E was used in reflected light. Dark field observations were performed with fixed oculars of 10× and objectives with different magnifications (5, 10, 20 and 40×). Cross-section photomicrographs were recorded with an Olympus DP70 digital scanner camera directly connected to the microscope.

Energy Dispersive X-Ray Fluorescence (ED-XRF)

X-ray fluorescence analysis (ED-XRF) was carried out using XRF Niton XL6t Gold+, used in the following modalities: silver anode; maximum voltage of the RX tube of 50kV, with the possibility to perform differentiated spectra at low (6kV), medium (20kV) and high (50kV) voltages in order to better differentiate the light elements from the heavy; measuring area: 3mm in diameter; acquisition time: variable from 60 to 120sec; detector: Peltier-cooled silicon multichannel, with beryllium window; detectable elements: $Z > 12$, i.e. from magnesium onwards.

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

SEM-EDS analyses were performed with a Jeol 6400 scanning electron microscope equipped with an Oxford (Link) EDS microanalysis system (15kV, 0.28nA, ~1mm beam diameter, 60s counting time). Elemental data were then obtained using the Oxforddb 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. 8nm of metallic gold on their surface (EMITECH K550 sputter coater).

Gas Chromatography - Mass Spectrometry (GC-MS)

The analytical procedure based on GC/MS used for the analysis of lipids, and proteinaceous fractions has already been described in literature and is a well-regarded technique

nowadays across the heritage science community for detection and identification of organic components of paintings [15, 16]. The procedure involves the separation of the fatty acids from the proteinaceous material.

The different fractions were analysed by means of a Focus GC (Thermo Scientific) equipped with a split-splitless injector, coupled to DSQ II (Thermo Scientific) with single quadrupole. The mass spectrometer was operated in the EI positive mode (70eV). The carrier gas was used in the constant flow mode (He, purity 99.995%) at 20mL/min. The chromatographic separation of searched components was performed by means of a fused-silica capillary column (RXI-5, Restek) with a 0.25 μ m (30 \times 0.25 \times 0.25 μ m) methyl-silicone (5% phenyl) film and the injector was used in splitless mode. The mass spectrometer was operated in the EI positive mode (70eV) and the mass range was from 40 to 500m/z. Chromatograms were acquired both in total ion chromatogram (TIC) mode and selected ion monitoring (SIM) mode.

Results and Discussion

The diagnostic campaign on colours, through XRF providing elemental in-situ characterization of distributed areas sampled over the painted layers, has brought to light a palette rather rich in pigments, all characteristic of the artist and already identified in many other works. In figure 2 the numbers indicate the points where the XRF measurements were made and table 1 reports the obtained results.



Fig. 2. The painting on canvas *The Wedding Feast at Cana* by Jacopo Tintoretto: the numbers indicate the points where the XRF measurements were made

The results obtained by XRF give preliminary indications of the pigment composition (table 1). They had the first indications of the presence of white lead, vermilion, lead tin yellow, blue smalt, natural Earths in different chromatic points.

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Table 1. Results by XRF technique

N	Color	Identified chemical elements and semi-quantitative estimates													Interpretation of analytical data
		Si	S	Cl	K	Ca	Mn	Fe	Co	Cu	As	Hg	Pb	Other	
1	Dark background /radiolucent area to study preparation	tr	+	+	+	++	tr	+++ +	-	-	-	-	+	-	Dark natural earths, perhaps little gypsum, traces of white lead and chlorides
2	Yellow-gray/drapery maybe altered	++ +	-	+	+	+++	-	+++ +	-	+++	-	tr	Ni ++ Bi +	Blue smalt, natural earth (?), traces of white lead and chlorides	
3	Brown/drapery probably darkened	++ +	-	+	+	++	-	+++ +	+++	-	++	-	+	-	Blue smalt altered, natural lands, little white lead, traces of chlorides.
4	Deep Blue/Unaltered color	++ +	++ +	+	+	+	-	+	+	-	tr	-	+++ +	Ni tr	White lead, probably ultramarine, blue smalt and chlorides at trace level
5	Yellow-orange/very bright color	-	++ +	tr	+	+	-	tr	-	-	+++ +	-	-	-	Orpiment and/or realgar, traces of chlorides
6	Bright Red	+	++ +	+	+	++	-	+	-	-	-	+++ +	+++	-	Vermilion or cinnabar, white lead, traces of natural lands and chlorides.
7	Incarinate	tr	++ +	+	-	+	-	++	-	-	-	++	+++ +	Sn +	White lead, vermilion, lead tin yellow, natural earths or ochres, traces of chlorides, white lead.
8	Incarinate	tr	++ +	+	-	+	-	++	-	-	-	++	+++ +	Sn +	White lead, vermilion, lead tin yellow, natural earths or ochres, traces of chlorides. white lead.
9	Black	-	++ +	++ +	+	++	-	++	-	+++ +	-	-	++	Ba tr Ti tr	Altered copper pigment (blue, verdigris or malachite), probably black charcoal, natural earths, traces of chlorides and non-original pigments (white barium, titanium white)
10	Dark Background	tr	+	+	-	+	+	+++	-	-	-	+	+++ +	-	Natural hearths dark, lead white, little vermilion, traces of chlorides
11	Dark Background	tr	+	+	+	+	-	+++	-	-	-	-	+++ +	-	Natural hearths dark, lead white, traces of chlorides
12	Blue-Green angle added	-	++ +	++ +	+	++	++	+++ +	-	-	-	-	+++	Ba +++	Prussian blue (?), barium sulfate, white lead, ochre and/or natural earths, chlorides
13	Yellow comparison with point 5	-	++ +	+	+	++	-	+	-	-	+++ +	-	-	-	Orpiment and/or realgar, traces of chlorides

All cross-sections were observed at SEM and analysed by EDS, to identify the chemical elements present and then to know the pigments. Of the five cross-sections studied we report the cross-section of sample B, taken from the incarnate of the face of the figure with the beard in the middle of the scene (Fig. 3).



Fig. 3. Point where it was taken the sample B: from the incarnate of the face of the figure with the beard in the middle of the scene

Observing the cross-section of sample B (Fig. 4), it is noted that the colour, without ground, is articulated on three overlapping drafts: the first two, consisting of pictorial materials similar but not equal to each other, the third is a very thin layer interposed with film of varnish and therefore certainly not original.

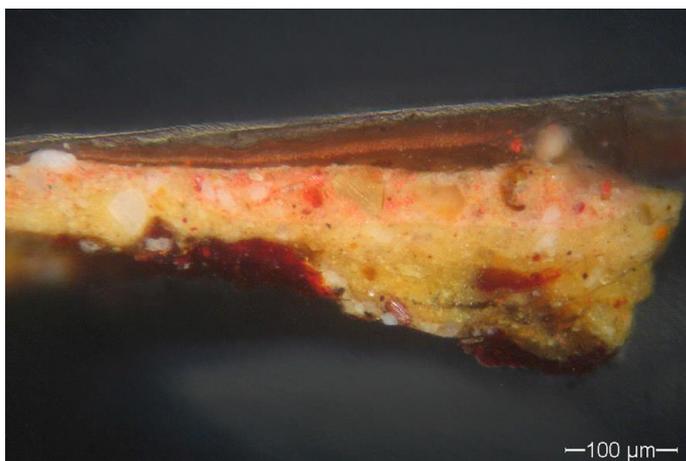


Fig. 4. Cross-section of sample B

The first layer is composed of a complex mixture of white lead, yellow ochre, red-violet lacquer and orpiment. The second contains always white lead and ochre, but the pink hue is due to the presence of vermilion particles.

The pigments identified in this sample are all compatible with the time of execution of the work, but a careful reading of the stratigraphy allows you to go a little further and formulate

hypotheses regarding the time of execution and the sense of these layers of painting. The two pictorial films, in addition to having very similar tonalities, are very well adherents so much that they appear (especially with the optical microscope) quite continuous among them. However, the SEM observations clearly show that the two layers are separated by a very thin dark film, evidently of organic nature (Fig. 5).

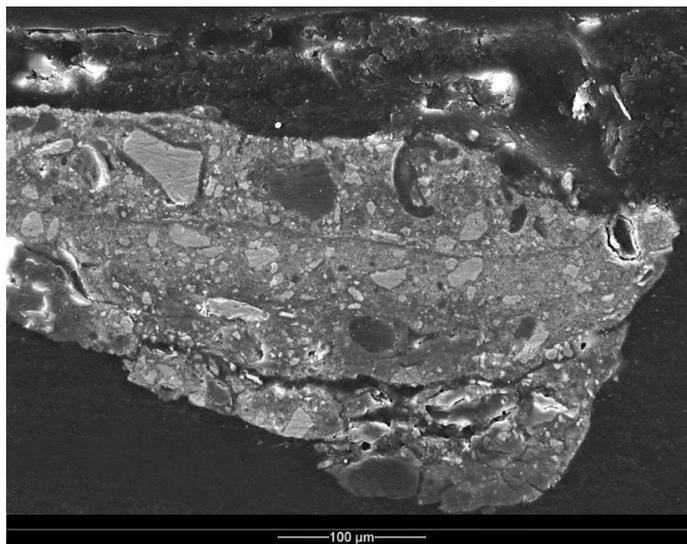


Fig. 5. SEM-SE (secondary electrons) image of the stratigraphic section of sample B

It is difficult to know whether it is a layer of varnish or simply an accumulation of organic binder. The fact is that this detail represents a clear discontinuity between the parties and makes it possible to affirm that the overlying draft has been applied on an already dry color. In practice, the hypothesis that there has been a corrective intervention of the incarnate of the portrait character is entirely plausible. Intervention carried out after some time assessed in the order of some years (at most a few decades).

From the overall study it was observed that the paint technique, as it emerges from the structure of the layers of colour, is quite characteristic of the artist: fast, with a few drafts of colour often almost melted among them, within which are very often present different pigments in mixture.

A very interesting aspect that emerges from the stratigraphic surveys is that the painting appears lacking a real preparatory draft and the colour seems to have been applied directly on the textile support. In all the cross-sections of the samples taken from the original areas of the canvas there are no traces, even minimal, of the traditional gypsum mixture and glue present instead in many other works of the Tintoretto [3-6]. This particular characteristic is in accordance with the fact that the weaving of the canvas is very clearly visible on the surface of the work. But above all it would explain why, in an old photographic image of the back of the canvas, taken before the last line, we see perfectly the painting whose colour, evidently, has gone through the meshes of the fabric precisely because of the absence of preparation. The retro picture of the painting *The Wedding Feast at Cana* by Jacopo Tintoretto (Fig. 6), during the restoration by Ferruccio Volpin of 1982 is now preserved in the archive of the Superintendence of Venice.

It has been seen that the only original white present is the white lead, used alone in lighter shades or in mixture with other pigments to lighten the tone. Another white pigment has also been identified, but that is certainly not original because it is present in the sky blue in the

upper left corner, i.e. in the added part. It is the barium sulfate, which is at that point mixed with another non-original pigment, like the Prussian blue. These two pigments allow having objective indications on the possible time of execution of the two angles, added at the top. In fact, if the Prussian blue was synthesized for the first time in Germany in 1704 and used in painting a few years later, the barium sulfate is even more recent. Barium sulfate as a natural mineral was known since the sixteenth century, but the earliest probable date for the introduction of natural barium sulphate into paints seems to be 1782-83. The artificial variant appears in the artist's palettes, with the name of barium white, only after 1830.

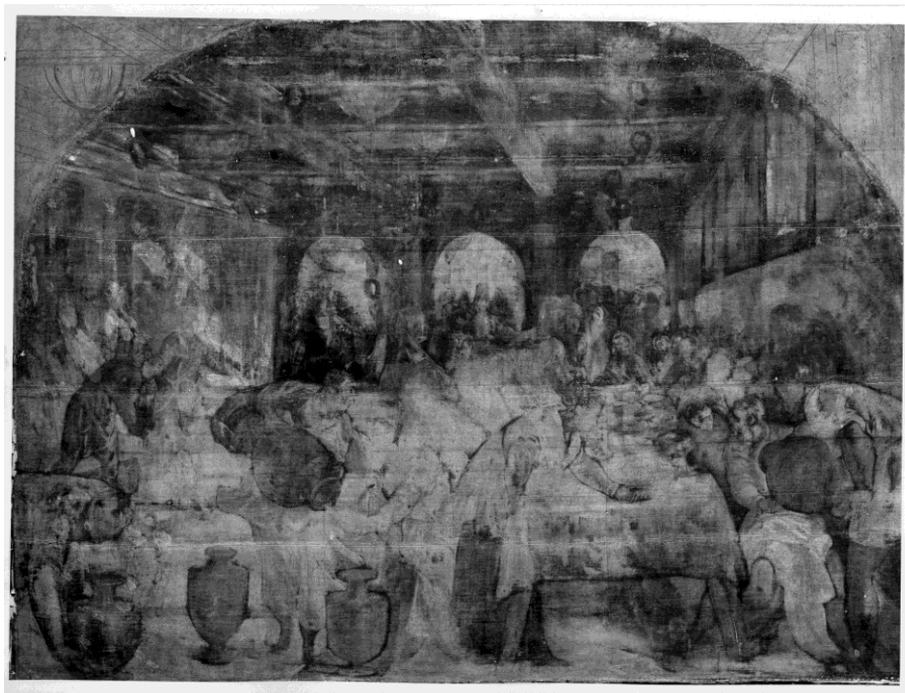


Fig. 6. Retro picture of the painting *The Wedding Feast at Cana* by Jacopo Tintoretto, during the restoration by Ferruccio Volpin of 1982. Photographic archive of the Scientific Laboratory of Venice

Yellows are three: the common ochre, the lead tin yellow type II (or Giallolino) and the orpiment. The ochre is always mixed with other colors to obtain intermediate hues, the Giallolino is in mixture with white lead and a bit of vermilion into the incarnate. The orpiment (sometimes mixed with realgar) is a rare and precious pigment, used with a certain frequency only by great Renaissance artists of Venice, composes the bright yellow-orange hues like that of the clear reflections of the robe of the character with the Beard in the lower left.

Red pigments are two: the ochre and the vermilion. The first is always present in mixture with other colours, while the second represents the main pigment of bright red colours or of the incarnate mixed with the white lead.

To make the various brown hues, more or less dark, the artist has always employed natural earths that have been, from time to time, darkened with a little black charcoal of vegetable origin (derived from the calcination of pieces of wood) or lightened with a little white lead or yellow ochre.

Greens are few and always composed of copper-based pigments: the verdigris and the copper resinate.

Of great interest is, finally, the nature of the blue pigments. They are still two, but they

have different importance and state of preservation altogether. They are the natural ultramarine, derived from the grinding of lapis lazuli, and the blue smalt. The first is a natural pigment, very old, precious and stable; the second is a cobalt-containing potash glass, more economical and widely used in European paintings from the end of the fifteenth century onwards.

In particular, the SEM-EDS results, obtained analysing the cross-section of sample E (from the dark brown of a male hair, in the background in the centre of the scene), showed a layer of white lead with several blue smalt particles inside, red-purplish masses of red lacquer and occasional fragments of black charcoal. Most of the blue smalt particles are transparent, but some have partially preserved the original blue-violet colour. The chemical analysis of fragments of blue smalt has provided the following results: SiO₂ = 84%, As₂O₃ = 6%, CoO = 4%, Fe₂O₃ = 4%, K₂O = 1%, CaO = 1%. The very low potassium content confirms the high degradation of this vitreous pigment [17].

It is, therefore, the further case of use of disposing in an improper context as the pigment is suitable almost exclusively in wall painting using an inorganic medium. Several studies have now shown, in fact, that in contact with organic medium dispose of it tends to react with the fatty acids of the binder forming potassium oiled and losing in fact the colour [17]. Being, moreover, a glass, has a refractive index so low that over time tends to become gradually less opaque.

Five samples of paint material were studied by gas chromatography coupled with mass spectrometry to search for the organic binding media (samples F, G, H, I and L). The investigations showed in all samples the presence of lipid and protein material. A first very interesting and unexpected result is that the lipid fraction detected is not attributable to a drying oil, allowing saying that the painting was not made with the oil technique, disproved the widespread and consolidated opinion of art historians who have always shared *The wedding feast of Cana* an oil painting.

In fact, we have seen the presence of azelaic (nonanedioic acid, saturated dicarboxylic acid), palmitic (C16:0), oleic (C18:1) and miristic (C18:0) acids, but in particular the ratio azelaic/miristic acid is much lower than one, thus excluding the presence of any siccative oil [18].

Table 2 shows the relative percentages of fatty acids in samples, A/P (azelaic/palmitic acid) and P/S (palmitic/stearic acid) ratios.

Table 2. Relative percentages of fatty acids in samples F, G, H, I, and L; A/P (azelaic/palmitic acid) and P/S (palmitic/stearic acid) ratios

Sample	Fatty acid				A/P	P/S
	Azelaic	C16:0	C18:1	C18:0		
F	17,54	50,42	2,20	29,54	0,35	1,71
G	20,11	40,13	3,02	27,89	0,50	1,44
H	13,11	41,64	2,88	33,73	0,32	1,23
I	10,01	52,80	1,94	32,42	0,19	1,63
L	14,48	39,21	3,00	33,60	0,36	1,17

It is also seen that all samples show the presence of the lipid and protein fraction of the egg, presumably yolk, and that two samples, presenting hydroxyproline (low signal), presumably contain animal glue, as a minority component.

The results obtained tell us that Tintoretto to paint the *Wedding at Cana* used mainly tempera technique, employing as egg binder, presumably yolk (Fig. 7), for the proteinaceous and lipid content determined, and not the technique that foresaw the use of drying oil, of which it was normally used. Of course, we cannot rule out that in other areas of the painting there may be oil finishes. However, it is certain that the structure of this Tintoretto's masterpiece is in tempera.

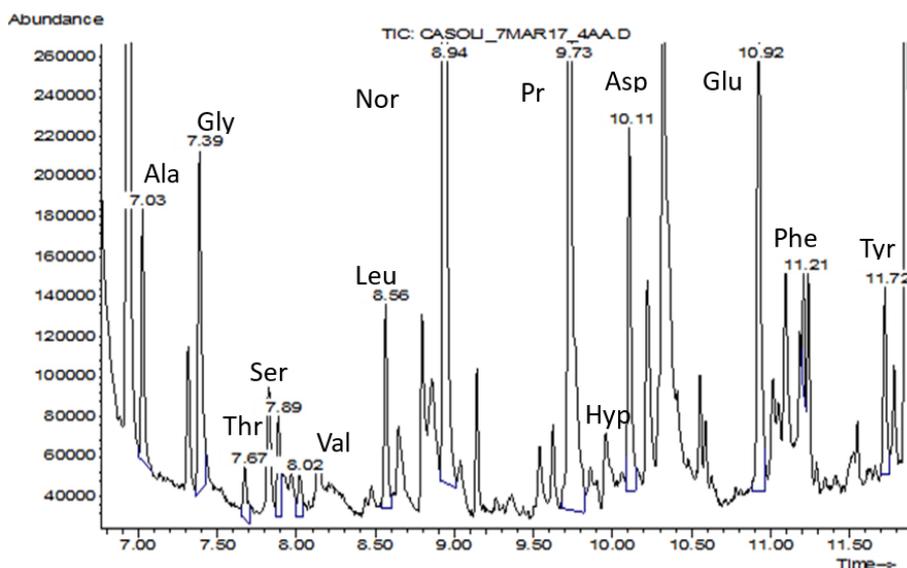


Fig. 7. GC/MS profile of the proteinaceous fraction of sample I: Ala = alanine, Gly = glycine, Thr = threonine, Ser = serine, Val = valine, Leu = leucine, Nleu = norleucine (internal standard), Pro = proline, Hyp = hydroxyproline, Asp = aspartic acid, Glu = glutamic acid, Phe = phenylalanine, Tyr = tyrosine

Animal glue, normally used as binder of the ground, which in this work is absent, is believed to be due to the restoration interventions which the framework has been subjected over the centuries, and in particular to the practice of the *Velinatura* of paint surface to protect it in handling operations.

Conclusions

The study of the paint *the Wedding Feast at Cana* by Jacopo Tintoretto was carried out, initially, using the non-invasive technique XRF, and led to a first indication of a palette rather rich in pigments. Based on the information acquired with the XRF analyses it was possible to guide the following sampling, reducing to a minimum the number of samples necessary for the chemical and stratigraphic investigations.

The first datum, which emerges from the stratigraphic surveys, is already quite surprising: the painting is without ground and the color layers were applied directly on the textile support. In all the samples taken from the original areas of the canvas there are no traces, even minimal, of the traditional mixture of gypsum and animal glue, present instead in many other works of Tintoretto.

The investigations revealed the existence of many pigments available at that time in Venice. That is to say the white lead, the lead-tin yellow type II (or Giallolino), the orpiment, the Vermillion, the Verdigris, the copper resin, the black charcoal of vegetable origin and the inevitable natural earths and ochre yellow and red. Of great interest is, finally, the nature of the blue pigments. They are two, but they have different importance and state of preservation altogether. They are the natural ultramarine, derived from the grinding of lapis lazuli, and the blue smalt or dispose of. It is, therefore, the umpteenth case of use of disposing in an improper context as the pigment is suitable almost exclusively in mural painting, conveyed with an inorganic medium. The identification of two pigments, one white and one blue, allowed to know the possible time of execution of the two angles, added at the top.

The pictorial technique, as it emerges from the structure of the layers of color, is quite characteristic of the artist: fast, with a few drafts of color often almost melted among them, within which are very often present different pigments in mixture.

This painting, generally described as an “oil on canvas”, proved to be basically an egg tempera, as the GC/MS analyses told us. Probably the numerous varnish layers applied over the color over the years have made glossy the pictorial surface tricking the art historians and causing a misinterpretation.

It is believed that the animal glue identified, normally used as a binder of the preparation, which in this work is absent, is due to the restoration interventions of which the picture was subject.

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