Received: 27 February 2021 | Accepted: 22 June 2021

DOI: 10.1111/arcm.12702

ORIGINAL ARTICLE

Analytical investigation of the original painted canvas of *Santa Irene*, by Giuseppe Verrio (Church of Sant'Irene, Lecce, Italy)*

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Abstract

The object of this study is unusual for both its material and technique. It is an oil painting on sheets of paper glued to a canvas made of linen fibres, thereby showing some execution peculiarities. It depicts the Virgin of Thessalonica in a hieratic attitude. The painting is attributed to the Salento-born artist Giuseppe Verrio (1639) for the church of the Theatine religious Order in Lecce, Italy, in which it is still placed, on the left altar of the transept. To truly understand and appreciate a work of art, it is important to have a basic knowledge of the materials and techniques used by the artist. For a better understanding of the execution techniques and to study the original materials and those that have been added over time, the painting was examined using the following analytical techniques: microscopic examination of cross-sections, μ-Raman spectroscopy and pyrolysis gas chromatography-mass spectrometry (Py-GC-MS). The data indicate that Verrio used different earthy, mineral and manufactured pigments, an organic dye used only on the paper, oil as a binder, and varnish as a protectant. The results demonstrate that the latter are both original and due to a subsequent restoration.

KEYWORDS

archaeometric analysis, binders, optical microscopy, painting, paper, pigments, Py-GC-MS, Raman spectroscopy

INTRODUCTION

Conservators and art historians need a deep understanding of the materials used, especially the pigments and painting techniques, in order to select the proper conservation procedure and to reconstruct an artist's workshop practices. Non-invasive examination methods are preferred since sampling is rarely allowed in paintings.

The object of this study is the canvas of "*S. Irene*", made in 1639 by Giuseppe Verrio (Figure 1). It is an extraordinary work of art, given the unusual construction and painting techniques used by the artist (Cassiano, 1995). It reflects, in all her beauty, the devotion and respect that the people of Lecce had for their patroness.

The artist used 19 sheets (2451 cm^2) of paper plus four smaller sheets (1892 cm^2) applied along the upper edge. Given the considerable size of the painting (43,350 cm^2 in total) we think that Verrio conceived it as a processional banner or gonfalon. At that time religious iconography considered saints as non-narrative images only to be venerated. They were generally represented standing or enthroned as protectors of brotherhoods or cities. This is the case of the glorious Virgin and Martyr St Irene, considered the patroness of Lecce until the second half of the 17th century (Foscarini & Vetrugno, 2000).

FIGURE 1 Sampling points on the painting Santa Irene

The authors of this paper carried out a series of scientific micro-invasive analyses in order to obtain information on the technique, pigments, conservation problems and effects of earlier attempts to restore the painting. The originality of the painting strongly motivated the authors to work on a little-known work of art through a study of the sources, scientific laboratory analysis, and the verbal and practical contribution of the restorers to whom it was entrusted. The last restoration was carried out in the laboratory of the Provincial Museum 'Sigismondo Castromediano' in Lecce, Italy.

A careful observation allowed for the discerning of a fairly stable pictorial film, altered and clouded by thick paint. The frame (44,973 cm^2) looks like a 19th-century addition, while an old reinforcing canvas, dated to the 1950s, was removed. After a consolidation of the back with Plexisol B550 (6% in nitro diluent), the painting was reupholstered with synthetic canvas and Beva371 on a hot vacuum table. The choice of the material to consolidate the canvas meets two main requirements: being reversible, in order to allow its possible removal, and not altering the colours of the painting. The support showed deformations, in particular along the edges, due to the repeated fixing on the frame, while the paper revealed bubbles, tears, lifts and gaps, some of which had previously been compensated with cellulose pulp. Numerous repaintings and a layer of old paint covered with a slight deposit of dust were found as well. The grouting of the gaps was carried out with carboxymethylcellulose, compatible with the original paper material. Cleaning was performed with non-aqueous solvents. After integrating the gaps with watercolour paints, a pictorial retouching was carried out and a retoucher varnish based on acrylic and ketone resins was applied (VV. AA., 2006). The multi-step non-invasive analytical protocol involved the following methods:

- Optical microscopy: Aimed at supporting and clarifying the spectroscopic results, assessing the conditions of the paint layers, documenting damage and suggesting the presence of pigment mixtures, layers and alteration compounds. A microscope is often used to identify pigments, mediums and the order of paint application with magnification ranges of 10–100×.
- µ-Raman spectroscopy: To identify the organic and inorganic materials used by the artist.
- Pyrolysis gas chromatography-mass spectrometry (Py-GC-MS): Allows for the acquiring of the fingerprint of the organic materials in paint samples: Pigments, binders and techniques used by the artist were determined and distinguished from latter, often undocumented, retouches.

MATERIALS AND METHODS

Sampling

During the cleaning phase, some microsamples were taken by the restorers of the 'Sigismondo Castromediano' Museum in Lecce to obtain an insight into the materials and techniques used by the artist Verrio to ensure correct choices would be made during restoration. The samples were taken with the use of scalpels and small forceps directly from defect areas of the painting where gaps and cracks where already present. The samples were all under 1 mg and come from several points, in compliance with the conservation criteria. Note that the choice was made to include only the most representative samples based on their readability (reference: the sky area in the upper left, ground area and underlying vegetation) (Figure 1).

Microscopic examination of the cross-sections

Three representative paper samples with adjacent layers were taken. The samples were embedded in Epothin epoxy resin. Microscopic analyses were made on cross-sections using a Nikon

ECLIPSE 80i optical microscope equipped with an X-Cite 120 fluorescence source, a high-sensitivity digital camera, and Nikon B-2A and UV-2A blocking filters, with the aim of making optical observations in visible, blue and ultraviolet (UV) light, while also checking for any fluorescent materials.

Micro-Raman spectroscopy

Raman spectroscopy is a non-destructive chemical analysis technique that provides detailed information about the chemical structure, phase and polymorphy, crystallinity, and molecular interactions of the material. It is based on the interaction of light with chemical bonds within a material. The μ-Raman spectroscopy analysis was performed using a Renishaw inVia benchtop instrument equipped with a double laser source, a diode laser and an He-Cd laser with excitation wavelengths of 785 and 442 nm, respectively, of a holographic notch (for line 785) and an EDGE filter (for line 442), a motorized *xy* phase, a Leica DMLM microscope with magnification objectives of 5×, 20× and 50× and with a spatial resolution of about 2 μm.

Radiation with a wavelength of 785 nm produced by a diode laser (maximum power pf 300 mW) was mainly used for excitation; only for green/blue minerals was the line 442 used to work at a beam energy of 10%. Neutral density filters were used to keep the laser power at a low level (0.1–2 mW) on the samples in order to avoid the photodecomposition of the pigments or unwanted heating effects, such as the transformations induced by the laser, occurring, for example, on Fe oxides and hydroxides.

The calibration of the spectrometer was checked using the most intense pure Si Raman peak at 520.5 cm^{-1}. The spectral resolution was 3 cm^{-1}. The baseline was subtracted in all spectra.

The samples were placed on a slide and mounted on a motorized *xy* table. The spectra of the examined samples were generally acquired using the 20× or 50× objectives, an exposure time of 20s, a variable spectral range typically between 100 and 1800 cm^{-1} for inorganic compounds, and three accumulations.

Py-GC-MS analysis

Samples were subjected to thermally assisted hydrolysis–methylation pyrolysis according to the procedure described above (Fico et al., 2018; Rizzo et al., 2021).

In brief, Py-GC-MS was carried out on a Curie point pyrolyser CPP (Pilodist, Germany) mounted on the injector of a 6890 N GC coupled with a 5973 inert quadrupole MS detector (Agilent Technologies). Prior to the Py-GC-MS analysis, samples (< 1 mg) were mechanically homogenized with 5 μL of tetramethylammonium hydroxide (TMAH) (2.5% in MeOH) to assist the hydrolysis and methylation of compounds and, after solvent evaporation at 60°C for 30–35 min, they were placed in ferromagnetic tubes closed at the lower end having the selected Curie point temperature. The pyrolysis conditions were as follows: Curie point temperature of 670°C, pyrolysis time of 9.9 s and pyrolysis chamber temperature of 200°C. Pyrolysate was separated on an HP-5MS column (i.d. of 0.25 mm, film of 0.25 μm, length of 30 m) with a 5 m deactivated silica pre-column, using the following GC programme: 50°C (13 min), increase of 5°C every 1 min until 290°C (10 min), split mode 1:2. Cycle time 2.94 scan/s, mass range *m*/*z* 50–550; high-purity He was used as carrier gas at initial pressure of 11.6 psi and constant flow 1.0 mL min^{-1}. The duration of the chromatographic run was 72 min. The data were analysed using MS Chemstation software (Agilent Technologies). The identification of the compounds was carried out by computer matching of the resulting mass spectra with the NIST mass spectral library or by comparison with mass spectra of known standards.

RESULTS AND DISCUSSION

A careful observation of the samples under the optical microscope preceded the analysis carried out with Raman spectroscopy. Such activity led to the preliminary knowledge of the samples through the identification and observation of some peculiar features.

The cross-section of sample SI1, taken from the lower centre, showed a layer of brown paper with a fragmentary and thin pictorial layer on the surface.

In sample SI2, taken from the bottom right, there were two pictorial layers on light blue paper. The first was yellow-pink while the second was green and paint had been applied to it (Figure 2).

Sample SI3, taken from the sky to the left of the patroness, revealed a more complex stratigraphy. The paper here is brown, probably due to the absorption of organic substances from the adhesive and a paint binder. A blue layer of paint was applied to the paper layer. The examination under UV light showed a fluorescent layer over some parts of this pictorial layer as well as on the surface.

In the three samples there was no trace of a preparatory layer.

Micro-Raman spectroscopy was applied to identify the pigments in the painting palette, identified by comparing the acquired spectra with those of the reference databases and with data present in the literature (Figure 3 and Table 1).

The analyses were carried out on different points of the pictorial layer through different samples. Indigo, an organic dye, was used for the light blue sheets of royal paper (Figure 3). There were also some red fibres that contained alizarin, the main constituent of the dye produced by *Rubia tinctorum*.

Among the pigments distinguished in sample SI2 were the yellow stannate of Pb (II) (type II, Pb [Si,Sn]O) with peaks at 137 and 324 cm^{-1} together with carbon black (about 1325–1580 cm^{-1}) (Figure 3). In the same sample there was a small percentage of white lead (basic Pb carbonate, $2PbCO_3$ Pb $[OH]_2$) and red ochre, a pigment based on hematite (α-Fe_2O_3), that is, a mineral based on Fe oxide (about 224–610 cm^{-1}).

In sample SI3 there was azurite (basic carbonate of Cu (II) $2CuCO_3 \cdot Cu(OH)_2$) in the blue; the characteristic peaks of azurite were located at 250, 403, 767, 839, 1098, 1432 and 1580 cm^{-1} (Bell et al., 1997; Burgio & Clark, 2001; Caggiani et al., 2016; Castro et al., 2005; Vandenabeele et al., 2000).

In addition, in the pictorial layer there was also yellow ochre and the widespread presence of vermilion crystals. Vermilion is a red pigment originally obtained from the powdered mineral cinnabar. The calcite detected was probably present as a filler on the paper itself.

In the green pictorial layer, a Cu resinate was detected. Such pigment was obtained by heating verdigris (Figure 4) with Venetian turpentine or boiling verdigris with linseed oil and turpentine (which is extracted from the resin) (Cennini & Frezzato, 2009).

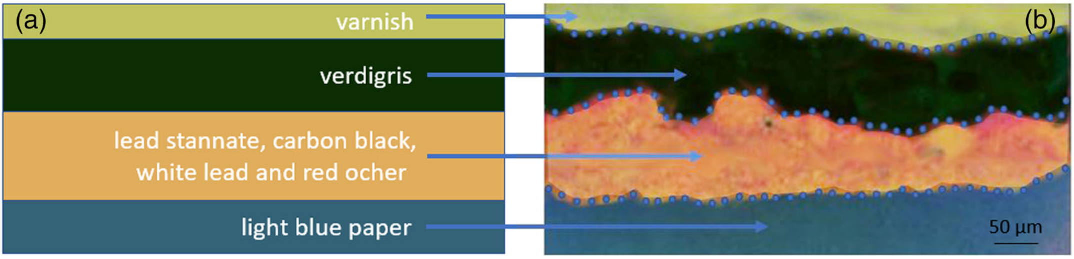

FIGURE 2 Cross-section of sample SI2: Scheme of stratigraphy (a) and stratigraphical reconstruction of the optical microscope image (b)

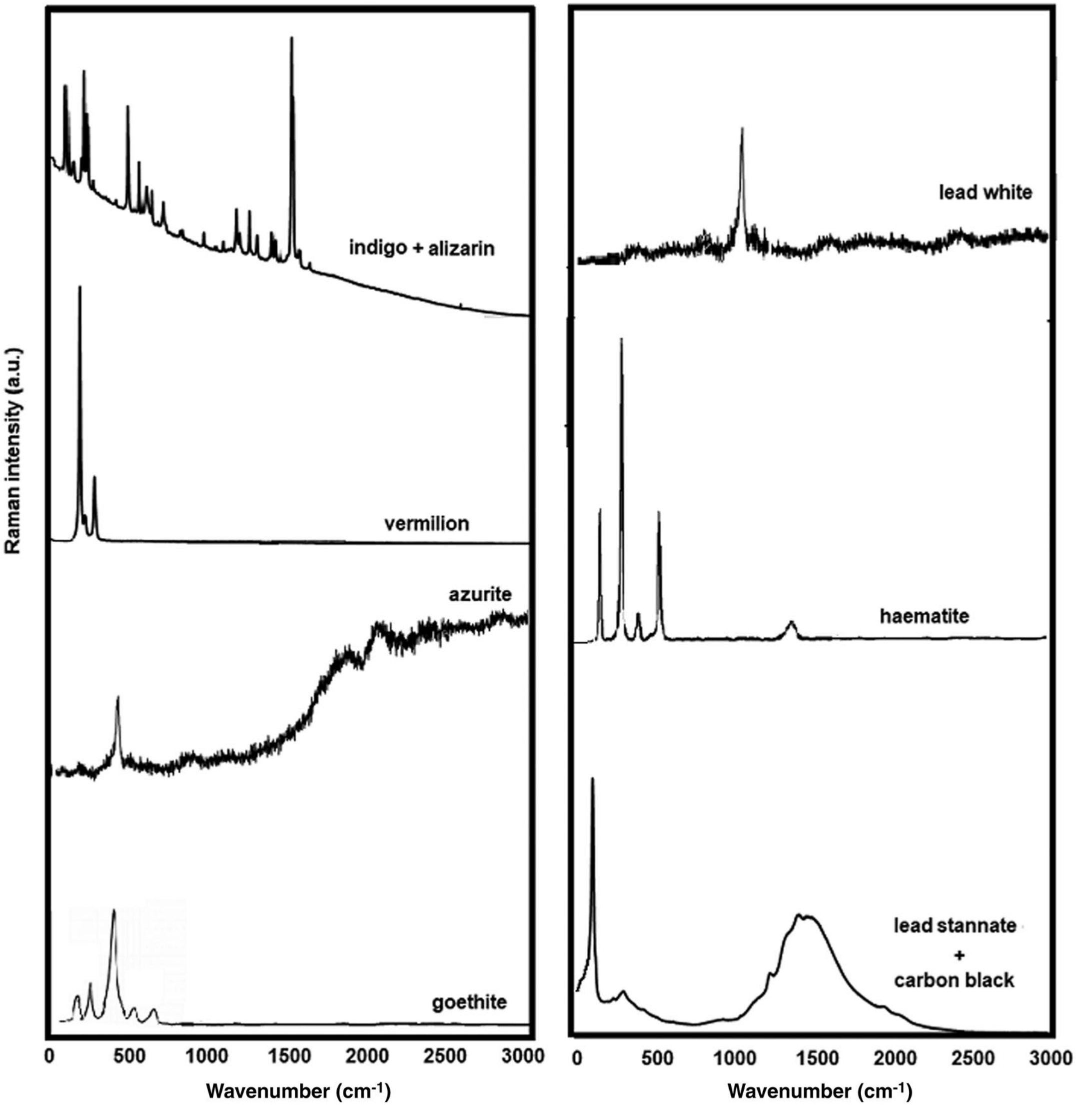

FIGURE 3 Micro-Raman spectra of the pigments found in the samples: Indigo and alizarin (light blue sheets of royal paper), lead white, hematite, Pb stannate and carbon black (pictorial layer of sample SI2), vermilion, azurite and goethite (pictorial layer of sample SI3)

The precise identification of which type of organic substance is present in a matrix or substrate requires the use of a methodology that provides a more specific response, and for this Py-GC-MS was used.

Analytical pyrolysis is a powerful technique used for the analysis of complex, heterogeneous organic materials which is based on the controlled thermal degradation of the sample in an inert atmosphere. The identification of the pyrolysis products is facilitated by means of their mass spectra, which is accomplished by Py-GC-MS. Since pyrolysis can be performed using very small sample amounts (< 1 mg) and does not require chemical pre-treatments, Py-GC-MS has been largely applied in the field of art conservation to identify binding media and protectives.

Pyrolysis of painting layers in the presence of TMAH produced a series of methylated compounds.

TABLE 1 Raman peaks of pigments identified in the samples

Pigment	*Primary element(s)*	*Wavenumber (cm^{-1})*	*Sample*
Indigo + alizarin	Organic	253, 599, 1226, 1572 + 239, 485, 841, 1189, 1482	Sheets of royal blue paper
Lead tin yellow (type II) + carbon black	Pb, Sn, Si + C	137, 324 + 1325, 1580	2
Azurite	Cu	1095, 936, 840, 760, 399, 330, 283, 246, 238, 179	3
Goethite (yellow ochre) + vermilion	Fe + Hg, S	205, 242, 297, 394, 477, 546, 1006 + 350, 343, 287, 253	3
Hematite (red ochre) + lead white	Fe + Pb	224, 243, 290, 299, 408, 495, 609 + 1051, 1055	2
Verdigris	Cu	179, 227, 320, 946 206, 708, 1296, 1442, 1611	2

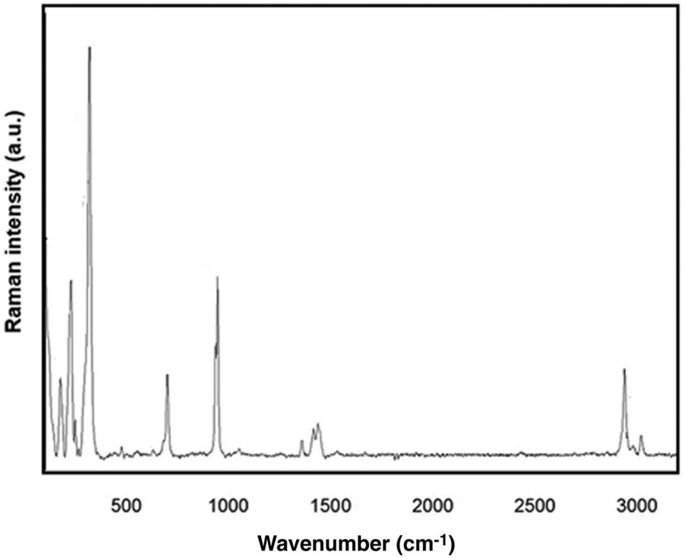

FIGURE 4 Micro-Raman spectra of verdigris

Py-GC-MS analyses allowed for the identification of the presence of animal glue in all layers, because pyrroles are abundant. Pyrroles (*N*-methylpyrrole, pyrrole, 2-methylpyrrole, 3-methylpyrrole and diketodipyrrole) and toluene were selected as markers of proteins. Pyrrole and diketodipyrrole are thermal degradation products of hydroxyproline. The latter is derived from the cyclization and dehydration of the dipeptide hydroxyproline–hydroxyproline. All were found in the three samples analysed (Chiavari et al., 1993).

In addition, all the paint layers were based on linseed oil. Table 3 lists the fatty acids, in particular the methylated dicarboxylic acids formed with the ageing of the oil-based binder. In this case it is linseed oil because the ratio between the methyl esters of palmitic and stearic acid (*P*/*S*) varies between 1.4 and 1.8, while the azelaic/palmitic acid ratio (*A*/*P*) varies between 0.8 and 2.0, along with the sum of dicarboxylic acids (ΣD) that is about 27% (the presence of a drying oil) (Cappitelli et al., 2002; Chiavari et al., 1998; Colombini & Modugno, 2009; Fabbri et al., 2000; Jun-Kai et al., 1997).

Finally, another interesting aspect common to all the analysed samples was the presence of a natural oxidized triterpenoid resin. Natural resins are commonly used as protective layers, adhesives and varnishes because they are sticky and hydrophobic. Chemically, natural resins are complex mixtures of terpenoids and their derivatives.

By comparing the literature data (Figure 5 and Table 2), we can argue that it is dammar resin, whose characteristic marker is ursonic acid; but we also detected dammarane-type triterpenoids (Bonaduce et al., 2016). Dammar resin is the general name given to a group of natural triterpenoid resins exuded by trees of the Dipterocarpaceae family and it is a mixture of tetracyclic compounds of the dammarane series and of pentacyclic compounds derived from ursonic acid. The main peaks were identified and are shown in Figure 5. The oxidized dammar resin-based paint most likely dates to the restoration carried out in the 1950s.

In sample SI2, abietic and neoabietic acid were detected, as well as other oxidized diterpenic acids, which together with epimanool, larixol and larixyl acetate constitute marker molecules for Venetian turpentine (*Larix decidua*) (Pastorova et al., 1997; Scalarone et al., 2002; van den Berg et al., 2000).

In sample SI3, in addition to animal glue, there is oxidized linseed oil ($P/S = 1.8$; $A/P = 0.9$) as well as a natural diterpenoid resin, which is also oxidized; the latter was identified thanks to the predominance of abietadiene acids and their degradation products (Figure 6 and Table 3).

A typical pyrogram obtained from pyrolysis/methylation of painting layers is depicted in Figure 6, which shows the components of the Pinaceae diterpenoid resins, in particular Venice

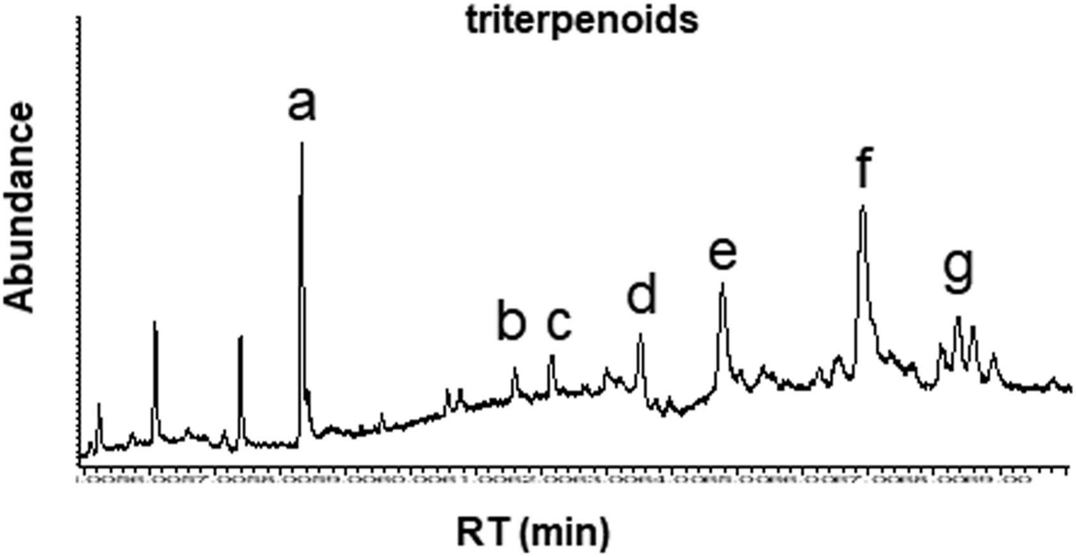

FIGURE 5 Total ion current (TIC) of pyrolysis gas chromatography-mass spectrometry (Py-GC-MS): Dammar resin markers identified in sample SI1

TABLE 2 Main triterpenoids identified in the pyrograms obtained

Peak	*Compound*	*Molecular weight*
a	Dammaradienone	424
b	Nor-β-amyrone	410
c	Dammaradienol	408
d	Nor-α-amyrone	410
e	Hydroxydammarenone	442
f	20,24-Epoxy-25-hydroxy-dammaren-3-one	458
g	Ursonic acid	468

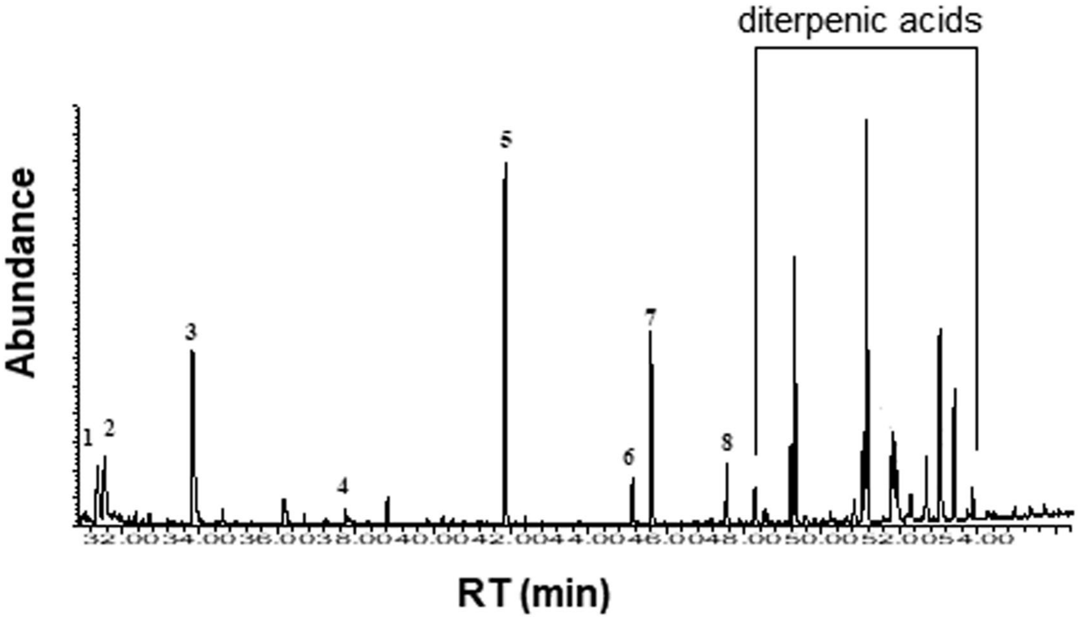

FIGURE 6 Pyrogram of sample SI3 and identified compounds

TABLE 3 Compounds identified in the pyrogram of sample SI3

Peak	*Compound*	m/z	*Sample 1*	*Sample 2*	*Sample 3*
1	Suberic acid, dim.e.	202	Yes	Yes	Yes
2	Lauric acid, m.e.	214	Yes	Yes	Yes
3	Azelaic acid, dim.e.	216	Yes	Yes	Yes
4	Sebacic acid, dim.e.	230	Yes	Yes	Yes
5	Myristic acid, m.e.	242	Yes	Yes	Yes
6	Palmitic acid, m.e.	270	Yes	Yes	Yes
7	Oleic acid, m.e.	296	Yes	Yes	Yes
8	Stearic acid, m.e.	298	Yes	Yes	Yes
9–21	Pimaric acid, m.e.	316		Yes	Yes
Diterpenic acids	Isopimaric acid, m.e.	316		Yes	Yes
	Dehydroabietic acid, m.e.	314		Yes	Yes
	6,8,11,13-Abietatetraenoic acid, m.e.	312			Yes
	7-Oxo-DHA, m.e.	342		Yes	Yes
	7-Hydroxy-DHA, m.e.	330		Yes	Yes
	8,11,13,15-Abietatetraenoic acid, m.e.	340			Yes
	15-Hydroxy-7-oxo-DHA, m.e.	344		Yes	Yes
	15-Hydroxy-DHA, m.e.	330		Yes	Yes
	7-Oxo-8,11,13,15-abietatetraenoic acid, m.e.	340			Yes
	5-Methyl-7-oxo-DHA, m.e.	356			Yes
	15-Methoxy-7-oxo-DHA, m.e.	372			Yes
	7,15-DimethoxytetraDHA, m.e.	372			Yes

Note: m.e., methyl ester; and dim.e., dimethyl ester.

turpentine. It is therefore assumed that the paper was glued to the original canvas with a mixture of animal glue, oil binder and Pinaceae resin.

CONCLUSIONS

This research deals with an unusual painting, both for its technique and its history. A great deal of information about the making of the painting comes from the close observation of its surface.

The investigations carried out on the painting, through the combination of complementary analytical techniques, have provided new and interesting information on the materials and the techniques of execution used.

Among them, the most interesting features are as follows:

- The layer of indigo-coloured light blue paper was glued to the original canvas using a mixture of animal glue, linseed oil and diterpene resin.
- The pictorial layers were based on linseed oil and pigments such as azurite, indigo, verdigris, Pb stannate (type II), white lead, yellow and red ochre, vermilion, alizarin, and carbon black directly applied to the paper layer.
- The materials introduced in the previous restorations were dammar resin varnish and a lining adhesive consisting of animal glue and slightly oxidized lipid material.

Such results demonstrate that Verrio mastered various materials and techniques, and underline the exceptional value of the painting of *S. Irene*, whose characteristics make it unique of its kind. In fact, the painting is interesting for both its iconographic aspects and for stylistic ones.

To date, in this territory, other examples of this type have not been found. In the past there were only preparatory sketches made on paper or cardboard. Probably the artist used paper in order to be quick during the execution technique. The speed of execution was dictated by the fact that the saint shortly after would leave the post of patroness to Sant'Oronzo.

Infrared rays revealed the preparatory drawing during the execution of the operative phases of the conservative restoration. Under the painted surface, in correspondence with the detail showing the Porta Napoli, we observe a group of people who seem to cross the famous gateway door. This is probably an allusive act: The crowd accompanies the saint out of the city when she is ousted by Sant'Oronzo, her successor as patroness.

ACKNOWLEDGEMENTS

Special thanks to the restorers Mary Coppola and Nicola Ancona (Restoration Laboratory of Paintings and Canvases of the Provincial Museum 'S. Castromediano') for the useful information provided regarding the restoration work carried out. The authors also thank Dr Inez D. Van der Werf and Professor Giuseppe E. De Benedetto for putting their skills and tools at their disposal. Last, but not least, the authors are grateful to the Archiepiscopal Curia of Lecce for the authorization to use the photograph of the painting.

PEER REVIEW

The peer review history for this article is available at https://publons.com/publon/10.1111/arcm.12702.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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How to cite this article: Rizzo, D., & Casciaro, R. (2021). Analytical investigation of the original painted canvas of *Santa Irene*, by Giuseppe Verrio (Church of Sant’Irene, Lecce, Italy)*. *Archaeometry*, 1–11. https://doi.org/10.1111/arcm.12702