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A MULTI-ANALYTICAL APPROACH TO THE STUDY OF THE MURAL PAINTINGS IN THE PRESBYTERY OF SANTA MARIA ANTIQUA AL FORO ROMANO IN ROME*

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This paper presents the results of analyses carried out on three decorative phases of the presbytery of the church of Santa Maria Antiqua al Foro Romano in Rome: the fourth-century AD *mosaics setting bed; the Adoration of the Cross, dated to the papacy of John VII (*AD *705–7); and the paintings in the apse of the Pope Paul I (*AD *757–68) phase. The research allowed the characterization of the painting techniques, pigments, organic compounds and degradation products by means of a video microscope, optical microscopy, and μ-Raman and FT–IR spectroscopy, contributing to a better understanding of the changes in the techniques and materials used throughout the centuries in one of the most relevant medieval Christian monuments in Western Europe.*

KEYWORDS: ROMAN FORUM, MIDDLE AGES, WALL PAINTINGS, *IN SITU* INVESTIGATION, μ-RAMAN SPECTROSCOPY, FOURIER TRANSFORM INFRARED SPECTROSCOPY

INTRODUCTION

The church of Santa Maria Antiqua, located inside the Foro Romano in Rome and adapted from an Imperial Roman building, is a monument of the utmost importance for understanding the development of early medieval and Byzantine art in Rome.

The paintings hosted in this church represent the chronological sequence of a series of decorations painted at various times from the Imperial age until the ninth century AD. They are precious evidence of the stylistic, iconographic and technical choices made by patrons and masters in Rome between Late Antiquity and the Middle Ages.

This research is the outcome of a collaboration between the Università degli Studi di Parma and the Università degli Studi della Tuscia as part of the research project Santa Maria Antiqua, organized by the Università degli Studi della Tuscia and directed by Maria Andaloro from 2000, with the aim of studying the decorative phases of this monument from both an art-historical and a technical point of view.

Thanks to the complete restoration of the paintings in the church's presbytery (Fig. 1 (a)) in 2011 and 2012, a diagnostic survey campaign was carried out, focusing on the characterization of the materials of three specific phases: (1) the fourth-century AD remains of bedding mortars

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and plasters dating back to the mosaic decoration that covered the ancient *tablinum*, the area that at a later stage would have been transformed into the presbytery of the Christian monument (Fig. 1 (b)); (2) the *Adoration of the Cross*, painted on the triumphal arch and dated to the papacy

Figure 1 *(a) The presbytery of the church of Santa Maria Antiqua al Foro Romano. (b) The fourth-century remains of the mosaic decoration in the eastern wall. (c) The Pope John VII (705–7) Adoration of the Cross on the triumphal arch. (d) The Pope Paul I (757–68) paintings in the apse. © Università degli Studi della Tuscia (a, b) and Soprintendenza Speciale per i Beni Archeologici di Roma (b, c). [Colour figure can be viewed at wileyonlinelibrary.com]*

of John VII (AD 705–7), which was examined for the first time on this occasion (Fig. 1 (c)); and (3) the degraded paintings in the apse, dated to the decorative phase of Pope Paul I (AD 757–68), of which overpainted materials have been analysed (Fig. 1 (d)).

The diagnostic survey campaign included *in situ* investigations of the decorative phases by means of a video microscope and sampling of mortars and pigments for laboratory analyses. Optical microscopy, μ-Raman spectroscopy and diffuse reflectance infrared spectroscopy were carried out on the samples in order to characterize the mortars, original pigments and overpainted materials.

THE DECORATIVE PHASES

The fourth-century mosaics

The bedding mortars in the eastern wall of the presbytery of Santa Maria Antiqua analysed in the course of this study are related to the mosaic decoration that covered the ancient *tablinum* in the second half of the fourth century.

At that time, the walls of this area were coated with *opus testaceum* and decorated with *opus sectile*, while the vaults were covered with mosaics (Krautheimer *et al.* 1959; Romanelli and Nordaghen 1999). Today, the *opus sectile* survives in part and only a few tesserae are still *in situ*. However, traces of bedding mortars and plasters of the mosaic are still present, together with considerable traces of painted areas on the bedding mortars.

The patterns of the *opus sectile* are not easily recognizable due to the traces of plasters of later wall paintings applied on top. However, it is possible to establish a general layout: a marble base ran up to approximately 35 cm from the floor; on top, a moulded marble frame, of which traces are still visible, served as a partition from the upper decorative register, which was probably made of rectangular panels alternating with vertical fascias. Further up, a large band served as a link to the mosaics of the vaults (Guiglia Guidobaldi 2004). Traces of this band are still visible on the western wall, where both the remains of the painted bedding mortars and the tesserae's marks on the mortars allowed the reconstruction of its original pattern. The band was decorated with a motif consisting of two repeating mirrored red 'S' shapes, outlined by two further blue monochrome bands.

Along the vaults, a blue mosaic was laid on a light blue–greyish mortar, while red and yellow decorations ran along the walls of the *tablinum* (Valentini 2015).

This area was transformed in a presbytery at the end of the sixth century, during the conversion of the building into a church (Rushforth 1902).

The pope John VII decorative phase

The large painting *Adoration of the Cross*, in the triumphal arch, represents the core of a wide system of representations.

The decoration of the front wall of the apse consisted of horizontal bands outlined by white, red and black frames, from the walls next to the apse at the bottom up to the vault.

From the lower area, the decoration comprised a *velum*, an inscription with white letters on a red background, which allowed the attribution of the paintings to the decorative phase that took place during the papacy of John VII (705–7), and an area with figures of standing saints below a panel depicting papal saints. Amongst them there is the figure of Pope John VII, portrayed with a square light blue nimbus, a symbol of a living person.

Higher on the front wall, the space between the apse and the vault is covered by the extensive painting *Adoration of the Cross*. It stands as central piece of a broader system of representations depicting *Scenes from the life of Christ* on the side walls of the presbytery: on the left wall, the episodes that precede the Crucifixion, whereas on the right wall are the episodes that come after the death of Christ.

What still remains of the John VII painting *Adoration of the Cross* in the triumphal arch is just the right-hand portion of the scene.

In the central area, the figure of Christ crucified is portrayed, with dark hair, a dark beard and a cross nimbus. Only a section containing Christ's head, chest and one arm is preserved. The cross was lifted up on the cliff of Golgotha, of which a small portion survives lower down on the wall. To the right of the Golgotha, a crowd of adoring figures moves towards Christ. Higher on the wall there is an inscription 11 lines long, composed of white letters on a red background, which relates prophets' passages concerning the Passion taken from the Septuagint. Each passage starts with the related prophet's name.

The Cross is flanked on the right by St John, whose head and halo are still visible, while the Virgin was probably standing on the other side.

Above the inscription, on a light blue background, there is a crowd of angels, arranged over three rows. The robes worn by the angels on the left are red, while those worn by the angels on the right are white; the figures are drawn in profile while kneeling down before Christ, offering their hands with the palms upwards.

At the top right, the Cross is flanked by two seraphims, who look at Christ on a dark blue background. Eyes are drawn on the white wings of the seraphim to the left, while the seraphim to the right has red plain wings.

The technique used to paint the John VII paintings is *fresco*, in which white lime was used as an additional binder. The plaster was laid on the wall after the earlier wall decoration had been removed, from about 4.5 m above floor level up to the vault. It is possible to note the profiles of the *pontate*, which do not correspond to the narrative scheme. This element, together with the position of the scaffolding holes, suggests that the plaster was applied and decorated following three different stages.

After application of the plaster, snapped lines were used to mark the main compositional elements, the traces of which are still recognizable on the plaster. Pigments for the basic tones were then mixed with lime and laid on. Finally, shadows, highlights and details were painted (Nordaghen 1990; Andaloro 2015).

The pope Paul I decorative phase

The decoration of the apse is heavily deteriorated due to rising dump (Laurenzi Tabasso 2006); however, it still possible to recognize portions of the paintings commissioned by Pope Paul I (757–68).

At the centre of the apse is the substantial figure of Christ, with dark hair and a dark beard, wearing a white robe. A tetramorph, an angel with three pairs of wings and four heads representing the symbols of the four evangelists, is visible further to the right.

On the opposite side, a figure with a light blue squared nimbus is located next to a barely visible inscription. The inscription allowed identification of the figure as Pope Paul I, who moves towards Christ together with the Virgin (Bordi 2015).

A *velum* with rounded decorations runs alongside the lower portion of the apse.

The technique used for the paintings is, again, *fresco*, in which white lime was used as an additional binder (Mancinotti and Tomasi 1981).

Incised compass marks on the plaster are observable in Christ's halo and in the rounded decorations of the *velum*, while, beneath the paint layer, traces of a preparatory drawing made with red and yellow ochre are clearly visible.

The plaster in the decoration of the apse was laid on *pontate*, apart from the portrait of the pontiff, which was painted on *giornata* (Mancinotti and Tomasi 1981).

EXPERIMENTAL

At first, all the data related to the surveys carried out by the Soprintendenza Archeologica di Roma and by the Università degli Studi della Tuscia between 2000 and 2009 were reviewed, in order to get a clear idea about the state of the documentation of the decorative phases and to address the following diagnostic survey.

The experimental stage involved preliminary *in situ* analysis such as acquisitions by means of a video microscope with the aim of studying the painting technique, following a methodological approach that is particularly useful in the case of complex palimpsest wall paintings (Pelosi *et al.* 2016). The monitoring of the paintings over time and the assessment of possible pigment alterations related to the presence of salts and high levels of relative humidity was also performed as a relevant phase of the *in situ* investigations.

High-magnification images of all the main coloured areas were taken using a Keyence portable video microscope directly connected to a portable computer (Fig. 2).

The *in situ* video microscope investigation helped in the selection of the best sampling points for the laboratory analysis.

Chips of paint, chips of paint with micro-fragments of plaster and micro-fragments of plaster alone were taken. Slides were prepared in the first case, while cross-sections were prepared from the other samples according to the usual techniques (Fig. 3).

The paint samples and cross-sections were then observed and photographed under both visible light and UV light using a Zeiss Axioskop polarizing microscope equipped with a Zeiss AxioCam digital camera.

Subsequently, the samples were analysed by μ-Raman spectroscopy to characterize the inorganic materials, using a Jobin Yvon Horiba LabRam Raman micro-spectrometer, equipped with a confocal Olympus microscope with 10×, 50× and 100× magnifications, a 632.8 nm He–Ne laser, $2\,cm^{-1}$ spectral resolution and 1 μm spatial resolution. Pigments and other compounds were identified through μ-Raman spectroscopy, by comparing the obtained spectra with literature data (Burgio and Clark 2001; Bouchard and Smith 2003) and spectral databases (http://www.fis.unipr.it/phevix/ramandb.php; http://minerals.gps.caltech.edu/FILES/raman; http://rruff.info).

The samples were then analysed by Fourier transform infrared spectroscopy in diffuse reflectance modality (DRIFT) in order to characterize the organic materials present. The spectra were obtained using a Nicolet Avatar 360 spectrometer equipped with a DTGS detector and elaborated by using the OMNIC 5.2 software. The samples were grounded using spectrophotometric grade KBr (1% sample in KBr) in an agate mortar. The obtained sample/KBr homogeneous mixture was transferred on to the slide of the DRIFT accessory and measured. For each spectrum, 128 scans were recorded, with a resolution of $4\,cm^{-1}$ in the 400–4000 cm^{-1} spectral range. The spectrum of the KBr powder was used as background. No specular bands appeared during

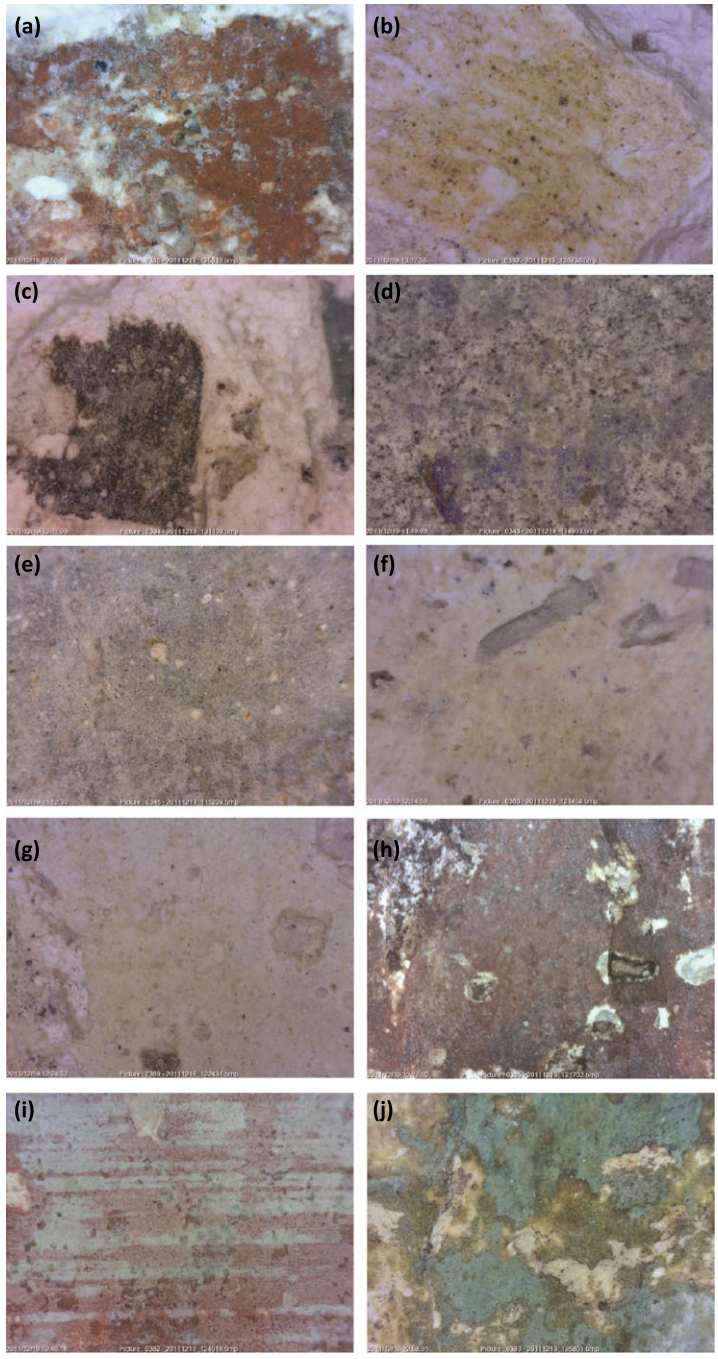

Figure 2 *Video microscope acquisitions of different areas, 50×: (a) red, (b) yellow and (c) black paint remains in the eastern presbytery wall. From the Adoration of the Cross scene: (d) dark blue background; (e) light blue background above the inscription; (f) the white fascia outlining the triumphal arch; (g) the white robe of the angel; (h) the light blue highlight of the brown robe worn by an angel; (i) the red and green background below the inscription; (j) the green cliff of Golgotha. [Colour figure can be viewed at wileyonlinelibrary.com]*

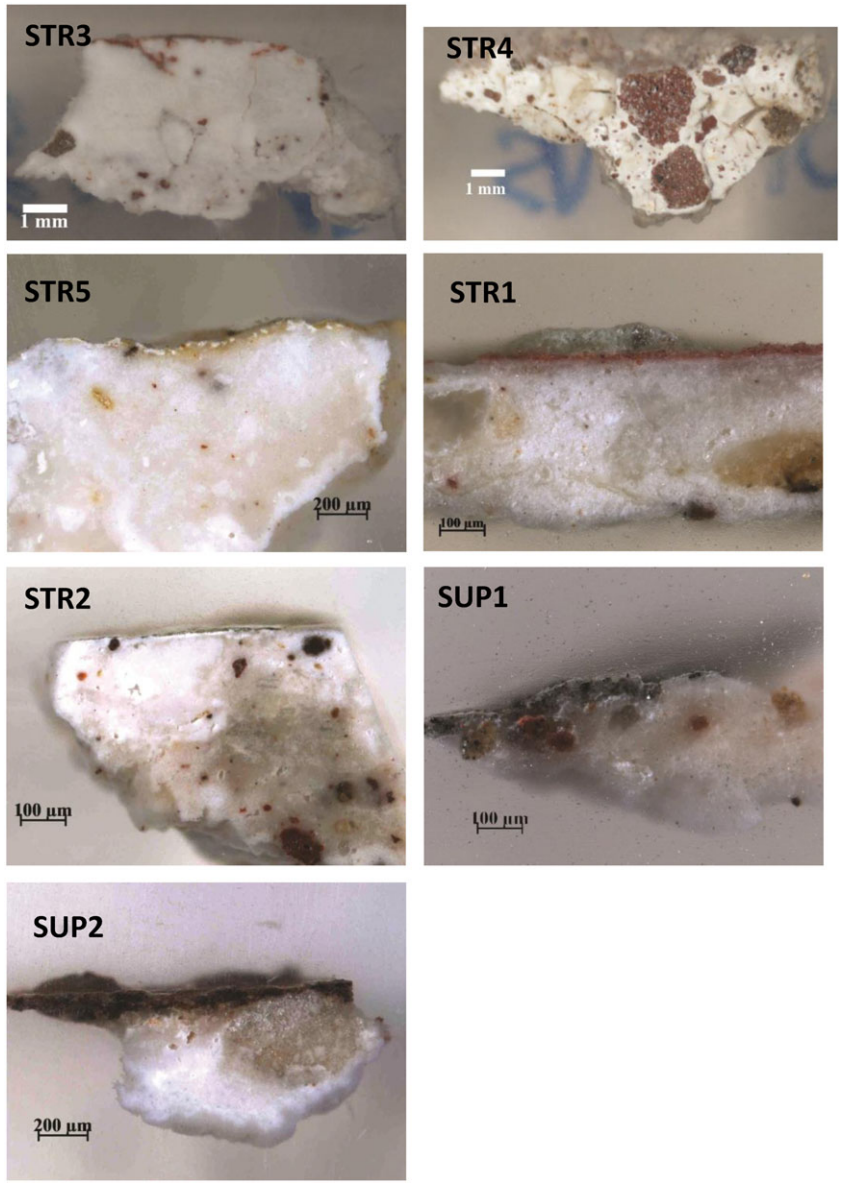

Figure 3 *Cross-sections of samples taken from the fourth-century bedding mortars (STR3, STR4 and STR5), the Adoration of the Cross scene dated to the papacy of John VII (705–7) (STR1, STR2) and the paintings in the apse dated to the decorative phase of Pope Paul I (757–68) (SUP1, SUP2). [Colour figure can be viewed at wileyonlinelibrary.com]*

acquisition of the spectra. The study and interpretation of the FT–IR spectra was accomplished by comparing the experimental results with literature data (Derrick *et al.* 1999; Adrover Gracia 2001) and spectral databases (IRUG Spectral Database, 2014 edition, http://www.irug.org; and other databases supplied with the Omnic software).

Finally, the gathered data were first elaborated and then contextualized in relation to earlier diagnostic surveys and art-historical research.

RESULTS AND DISCUSSION

Mortars and pigments from the fourth-century mosaics

Four samples were taken from the eastern presbytery wall: a micro-fragment of bedding mortar (sample STR4, Fig. 3), a chip of red paint with a micro-fragment of plaster (sample STR3, Fig. 3), a chip of yellow paint with a micro-fragment of plaster (sample STR5, Fig. 3) and a chip of black paint (sample PIG7).

The mortars

The samples taken were prepared as cross-sections and viewed under the microscope (Fig. 3): it can be noted that the mortar is white in colour in all cases and that the aggregate is present in different proportions and sizes.

A high content of poorly sorted aggregate particles is present in sample STR4 and the binder/aggregate ratio is 1:2. The aggregate is medium to coarse with highly spherical and subangular particles.

Samples STR3 and STR5 were collected from a red and a yellow painted area. In both cases, the aggregate is present in a very low percentage, less than 10%, with particle sizes ranging from 500 to 25 μm. The aggregate particles are poorly sorted, and have medium to low sphericity and a subangular profile in the first sample, while they are well sorted and have low sphericity and a subangular profile in the second one.

These morphological observations suggest that samples STR3 and STR5 may be related to the bedding layer where the tesserae were inserted, while sample STR4 may be representative of the deeper and coarser setting mortar underneath the bedding layer.

The results of the μ-Raman and FT–IR spectroscopy are summarized in Table 1 and in Tables S1 and S2. μ-Raman analysis allowed the identification of the binder as lime (calcite was consistently detected in all the samples analysed; see Table 1), while when it comes to the aggregate, minerals typically related to pozzolan, such as quartz, augite and analcime (see Table 1), were detected. Gypsum was also detected, on the upper area of the samples.

The pigments

High-magnification images of the red painted area from which sample STR3 was taken show a compact painted surface and crystals of calcite and black inclusions (Fig. 2 (a)).

The ochre paint from which sample STR5 was taken appears quite diluted, and black inclusions and yellowish particles can be distinguished (Fig. 2 (b)).

Sample PIG7 was taken from a black-painted area where the pigment is well absorbed in the plaster and reddish inclusions are recognizable (Fig. 2 (c)).

Under the microscope, the paint layer in samples STR3 is bright red and orange, and small black inclusions can be observed (Fig. 3). In sample STR5, the paint layer is ochre with orange and small black particles (Fig. 3).

Goethite, hematite and carbon have been identified by Raman spectroscopy in the paint layers of samples STR3 and STR5 and in sample PIG7 (see Table 1). The presence of paint in the mortars is consistent with the practice of painting the bedding mortars that had to host the tiles, to adapt the colour of the mortars to that of the tiles (Roccasecca 1990).

Table 1 *Compounds identified by Raman (R) and FT–IR (IR) analyses*

	Compounds identified
Samples from the fourth-century bedding mortars	
STR3	Calcite (R), gypsum (R), analcime (R), augite (R), hematite (R), goethite (R), carbon (R)
STR4	Calcite (R), gypsum (R), analcime (R), augite (R), hematite (R)
STR5	Calcite (R), gypsum (R), quartz (R), hematite (R), goethite (R)
PIG7	Hematite (R), goethite (R), carbon (R)
Samples from the Adoration of the Cross scene	
STR1	Calcite (R), analcime (R), gypsum (R), apatite (R), quartz (R), hematite (R), carbon (R)
STR2	Calcite (R), hematite (R), anatase (R), celadonite (R), gypsum (R)
PIG1	Calcite (R), carbon (R), Egyptian blue (R), lazurite (R)
PIG2	Calcium carbonate (IR), calcite (R), carbon (R), lazurite (R), gypsum (R, IR), wax (R, IR)
PIG3	Calcium carbonate (IR), carbon (R), hematite (R), wax (R, IR), gypsum (R, IR), an acrylic compound (IR)
PIG4	Calcite (R), gypsum (R), hematite (R), whewellite (R)
PIG5	Calcite (R), gypsum (R), carbon (R), hematite (R), goethite (R)
PIG6	Carbon (R), Egyptian blue (R), lazurite (R)
SUP3	Beeswax (IR), gypsum (IR), oxalate (IR)
Samples from the overpainted materials in the apse	
SUP1	Calcium carbonate (IR), calcite (R), gypsum (R, IR), hematite (R), carbon (R), a proteinaceous compound (IR), an acrylic compound (IR)
SUP2	Calcium carbonate (IR), calcite (R), gypsum (R, IR), carbon (R), hematite (R), goethite (R), vanadinite (R), lazurite (R), a proteinaceous compound (IR), an acrylic compound (IR)

The pope John VII phase

Based on *in situ* observations, eight pigment samples were collected from the main painted areas of the *Adoration of the Cross* and two of them also included a micro-fragment of mortar.

The mortars

The mortar in sample STR1 and STR2 features about 20% of aggregate, with particle sizes ranging from 260 to 30 μm. The aggregate particles are moderately sorted, and have medium sphericity and a subrounded profile (Fig. 3).

μ-Raman analysis of the samples allowed the identification of lime as the binder (calcite was consistently found in both samples; see Table 1), while when it comes to the aggregate minerals typically related to pozzolan, such as apatite, analcime and anatase were detected (see Table 1).

The pigments

High-magnification images of the large white fascia that outlines the triumphal arch, from which sample PIG4 was collected, and of the white robes of the angels (sample PIG5), show that the paint is off-white in colour with small black inclusions and orange particles (Figs 2 (f) and 2 (g)).

μ-Raman analysis of sample PIG4 revealed the presence of carbon black, hematite, calcite, gypsum and whewellite, while in sample PIG5 calcite, gypsum, goethite, carbon black and hematite were identified (see Table 1). These results show that ochre was probably added to white lime in order to achieve a warmer shade.

With regard to the green areas, some differences were noticed between the green painted on top of a red layer in the background behind the group of people in the lower portion of the scene (sample STR1) and the green used to paint the cliff of Golgotha (sample STR2).

In the first case, the high-magnification images of the painted surface show that the green pigment was applied with thin brushstrokes over a red base (Fig. 2 (i)).

μ-Raman analysis revealed the presence of quartz, gypsum and calcite, while we were unable to detect any mineral that could be related to a green pigment (see Table 1).

In the second case, the high-magnification images show a compact painted surface consisting of greenish, black and orange particles (Fig. 2 (j)). μ-Raman analysis revealed the presence of celadonite, a characteristic mineral of green earth pigments (see Table 1) (Ospitali *et al.* 2008).

Even though no traces of green earth have been identified in sample STR1, the use of this pigment to paint the background of the scene cannot be ruled out. It might be present in a small quantity and its identification by Raman spectroscopy might be difficult.

The blue areas were painted using two different practices. High-magnification images of the light blue background above the inscription, from which sample PIG2 was collected (Fig. 2 (e)), show that the colour was obtained by superimposing layers of black and ochre pigment. The presence of carbon black was confirmed by μ-Raman analysis (see Table 1).

High-magnification images of the deep blue background in the upper part of the scene from which sample PIG1 was taken show that the blue hue was achieved by superimposing a thin blue layer on a black background (Fig. 2 (e)). μ-Raman analysis identified carbon black and Egyptian blue (see Table 1).

The same kind of mixture was detected on sample PIG6, taken from the light blue highlights of the brown robes worn by the angels (Fig. 2 (h)). High-magnification images of the area show the thin grey–blue layer painted over a dark blue base.

In addition to carbon black and Egyptian blue, lazurite, the mineral of which lapis lazuli pigment is composed, was detected in all the samples taken from the blue areas. Under the microscope, the lazurite particles looked uniform, small and round. These morphological features, together with the absence of minerals commonly associated with natural lapis lazuli, suggest that synthetic ultramarine blue pigment, developed in the 19th century, was probably used during a modern restoration treatment of the paintings.

Finally, hematite and carbon black (see Table 1) were detected in the samples collected from the red areas, the red background behind the group of people in the lower portion of the scene (sample STR1) and the red flames below one of the seraphims (sample PIG3).

Overpainted materials

Traces of overpainted materials were observed above the painted layers in two cases.

The first case was the sample taken from the deep blue background of the upper part of the scene (sample PIG2). The material, which looked like a small drop, had a glossy surface and measured less than 20 μm. μ-Raman analysis revealed the organic nature of the compound, its spectrum showing a good correspondence with that of beeswax (see Fig. 4 (a) and Table 1).

A portion of sample PIG2 was also analysed by FT–IR spectroscopy: gypsum, wax and some bands of calcium carbonate were detected (see Fig. 4 (b) and Table 1).

Overpainted materials were also observed in the sample collected from the red flames below one of the seraphims (sample PIG3). μ-Raman analysis revealed the organic nature of the compound in this case too (see Table 1). The FT–IR spectrum showed the presence of calcium carbonate, gypsum and an organic compound, probably of an acrylic nature (see Table 1).

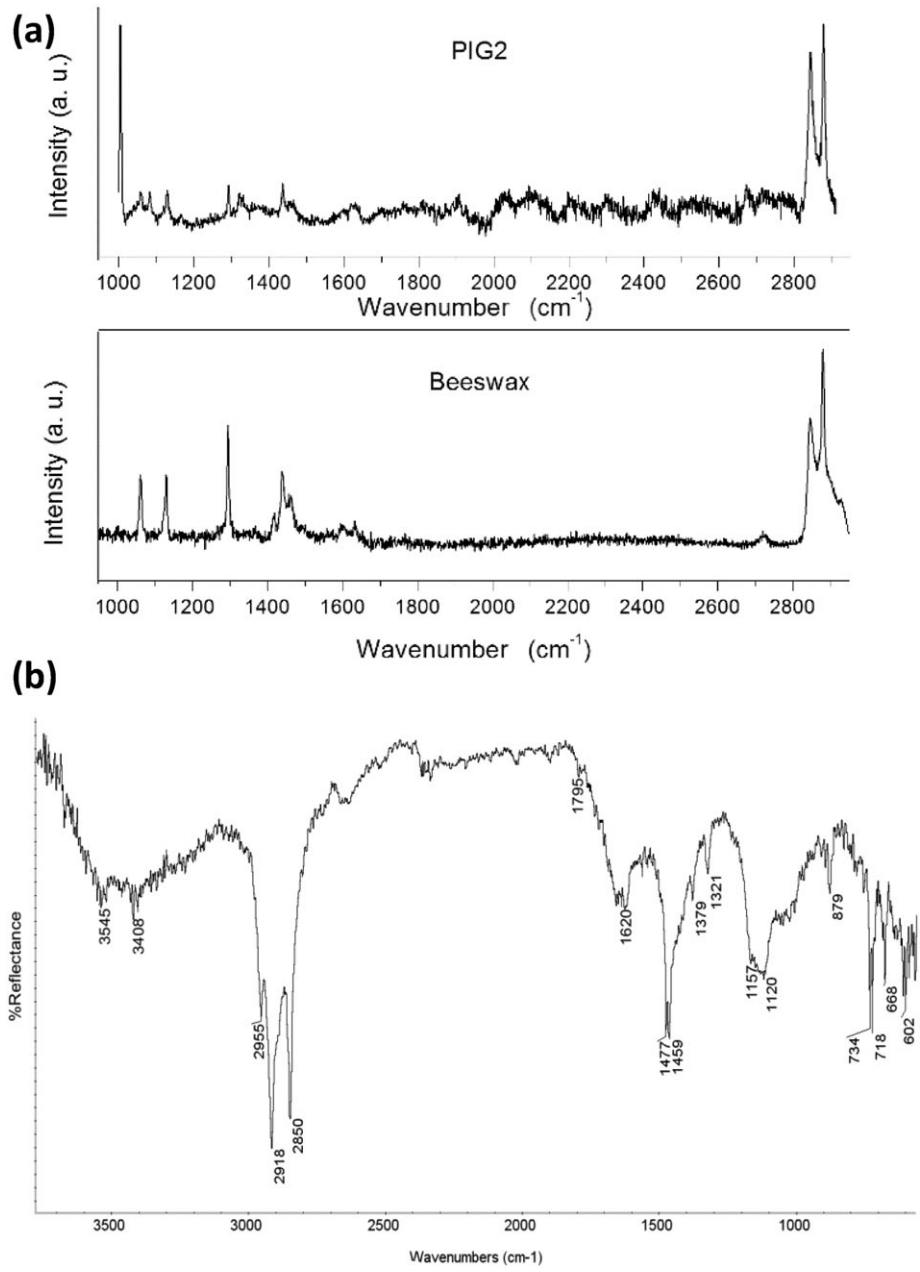

Figure 4 *(a) The Raman spectrum of the overpainted material analysed in sample PIG2 compared to the Raman spectrum of beeswax. (b) The DRIFT FT–IR spectrum of the same sample.*

The presence of an acrylic resin was supposed due to the bands at 2983, 2927, 2852, 1730, 1450, 1149 and 1030 cm^{-1}. Some bands are partially overlapped with those of sulphates and carbonates; therefore an infrared spectrum was measured on a sample fraction extracted with acetone, in order to confirm the presence of the acrylic resin. The match with the spectrum of Paraloid B72 confirmed the hypothesis that an acrylic resin is likely to be present (Fig. 5).

In addition, a sample was collected from an area characterized by thick spots of non-original material on the wall to the left of the apse (sample SUP3). Beeswax, traces of gypsum and oxalate were identified by FT–IR analysis (see Table 1).

The presence of wax is likely to be due to the treatments for aesthetic corrections carried out between 1901 and 1904, when a mixture of waxes and paraffin was applied on top of the surface of the paintings.

Oxalates were also detected in few areas of the paintings, and they might be related either to the degradation of these organic materials or, more probably, to the current or past metabolic activity of micro-organisms that have colonized the painting surface (Edwards *et al.* 1997; Torraca 2009; Zucconi *et al.* 2012).

Finally, it must be noted that calcium sulphate was frequently found on the superficial layers of many of the analysed samples. Its presence may be justified by the widespread use of cement-based consolidants applied during past restoration treatments. The very high values of relative humidity inside the church may have favoured the migration of the calcium sulphate contained within the cement. The exposure of the church to the urban atmosphere of Rome may also lead us to suppose that the gypsum is partially derived from sulphuric acid aerosols acting on the calcium carbonate phase of the paintings (Arnold and Zehnder 1991; Baglioni *et al.* 2003; Blaeuer and Rousset 2014).

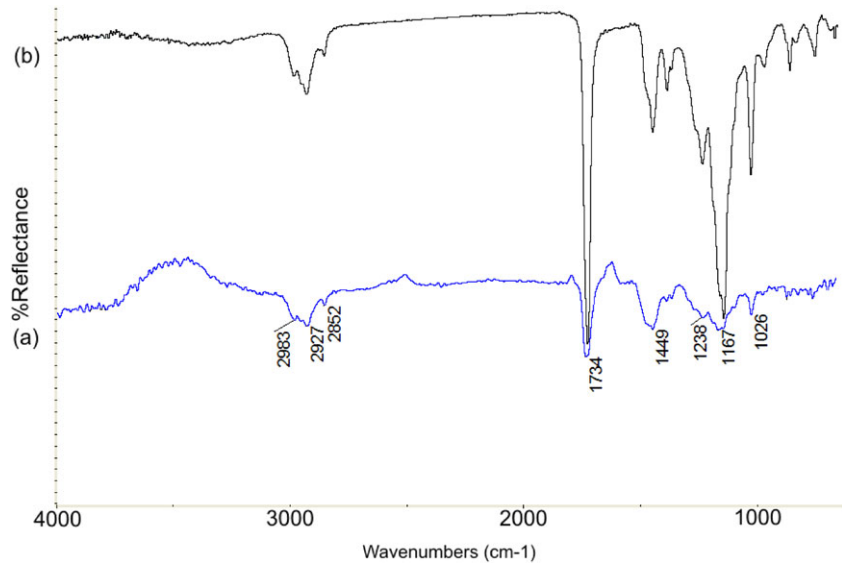

Figure 5 *The DRIFT FT–IR spectrum of a sample fraction extracted from sample PIG3 using acetone (a), compared to a spectrum of Paraloid B72 (b). [Colour figure can be viewed at wileyonlinelibrary.com]*

The pope Paul I phase

Since the analysis of these paintings had already been carried out during previous surveys, it was decided to collect only two samples from areas where deteriorated non-original materials were present.

The first sample (sample SUP1; see Fig. 3) was taken from an area of the sky that has not yet been restored. μ-Raman spectra revealed evidence of calcite, gypsum, carbon and hematite (see Table 1). FT–IR spectroscopy revealed the presence of calcium carbonate, gypsum and an acrylic material, with the same bands as shown for sample PIG3 (see Tables 1 and S2). These organic materials may be due to the treatment carried out by the Istituto Centrale del Restauro in 1955.

A second sample (sample SUP2; see Fig. 3) was taken from the wing of the angel on the right, retouched at the beginning of the 20th century by Tito Venturini Papari. μ-Raman analysis identified carbon, hematite, lazurite, goethite and vanadinite (see Table 1). Vanadium was indeed detected during previous surveys in many of the paintings retouched at the beginning of the 20th century. FT–IR spectroscopy revealed the presence of calcium carbonate, gypsum and an acrylic material (see Table 1). In this case also, the acrylic compound presented the same bands as for sample PIG3. Therefore, it can be confirmed that the same or a similar acrylic protective/consolidant was used during the past conservation treatments.

CONCLUSIONS

The study of the fourth- to fifth-century decorative phase, the Pope John VII paintings (705–7) on the triumphal arch and the degraded Pope Paul I paintings (757–68) on the apse of Santa Maria Antiqua in the Roman Forum allowed the characterization of the mortars, the pigments, the overpainted materials and the execution techniques.

The results allowed identification of the mortars as lime–pozzolan in all the three decorative phases, but with different lime-to-pozzolan ratios. Earth pigments were found on the mortar samples taken from the fourth-century phase, showing that they had been painted before applying the mosaic tiles. The technique used in the John VII paintings is *fresco,* in which lime white was used as an additional binder. Red ochre, lime white, green earth and carbon black were identified on the samples from this phase. The blue shades were obtained either by using a mixture of lime white and carbon black or by Egyptian blue alone. Non-original pigments and organic compounds were identified in samples from both the John VII and the Paul I phases, probably as a result of old conservation treatments and degradation. Calcium sulphate was detected in the superficial layers of many samples. This may be due to both the treatment of the paintings with cement-based consolidants, used during past restoration treatments, and the sulphuric acid aerosol-rich urban atmosphere of Rome to which the church is exposed.

The overall findings of the analyses carried out by the Soprintendenza Archeologica di Roma and by the Università della Tuscia between 2000 and 2011 in the presbytery area of Santa Maria Antiqua have allowed us to outline a scheme regarding the materials used in many of the decorative phases.

Lime–pozzolan mortars were constantly used between the fourth and the eighth century, except for the period between the early sixth century and the second half of the seventh century, when lime–sand mortars were used instead. The plasters from the seventh century onwards are characterized by a high percentage of lime and by the presence of plant fibres (Pasquali 2008; Amato 2012). This particular composition, which is rather unusual for Rome, confirms the

Byzantine tradition or even the Eastern provenance of several workshops involved in the decoration of the church.

All the paintings were rendered as frescoes, and lime white was used as an additional binder. The pigments used prove to be rather consistent all over the period considered. They were mainly earth pigments for yellows and reds and either green earths or a mixture of carbon black and ochre for the greens. The blues were made using either Egyptian blue or a mixture of carbon black and lime white, the blacks were based on carbon and the whites were made using lime white (Pasquali 2008; Amato 2012).

The set of results obtained from this research sheds new light on the numerous studies performed earlier on the frescoes of Santa Maria Antiqua al Foro Romano, allowing us to have a better understanding of the changes in the techniques and materials used in the context of the Roman mural painting over the centuries.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

Table S1. Raman band assignments of the compounds identified.
Table S2. Results of FT–IR analysis.