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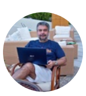

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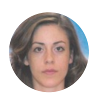

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The Byzantine wall paintings from the Protaton Church on Mount Athos, Greece: tradition and science

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Abstract

The present work is a study of the wall painting complex in the Protaton Church (1295) on Mount Athos, Greece. These paintings, high in artistic value, are themselves a monument—representative of the Macedonian iconographic style. What follows is historic data set against the results of analytical investigations: the fruit of extensive research aimed at determining precise details about the applied painting techniques for the wall paintings. Hitherto it has been held that what was traditionally defined as ''Byzantine fresco'' was executed only on wet plaster with limewater as the sole binding medium. Now, however, through the application of instrumental analytical investigations, it is possible to demonstrate that a mixed technique involving both *al fresco* and *al secco* was employed. Furthermore, it was determined, on the basis of results from gas chromatography–mass spectrometry (GC/MS), that egg together with a modest amount of animal glue were the organic binding media used for the Protaton art work. It is certain that the scenes were initially begun on wet plaster. During or even after drying the painting was completed using the aforementioned protein binding media, thanks to which a more resistant cohesion to the painted layers was secured.

Keywords: Artefacts; Animal glue; Binding media; Byzantine wall paintings; Egg; Fresco–secco; GC/MS; Protein

1. Introduction

The iconographic programme of the Protaton church, the oldest on Mount Athos in northern Greece, is the work of Manuel Panselinos (who ''shone like the moon''), an artist whose oeuvre became a point of reference not only for his contemporaries but also for many icon painters in later times (Acheimastou-Potamianou, 1994; Chatzifotis, 1995; Dionysios, 1996; Kondoglou, 1960; Maurommatis, 1999; Papaggelos, 1998; Tsigaridas, 2003). Although there are no historical data regarding Manuel Panselinos' life and artistic work, his name is referred by Dionysios of Fourna in his work *The Painter's Manual*, as the creator of the Protaton wall paintings, who came from Thessaloniki (Dionysios, 1996). Protaton, built in the tenth century, was repaired during the reign of Andronikos II Palaeologos (1282–1328). Its wall paintings were assigned to Panselinos, the finest representative of the Macedonian iconographic school, who should have been a painter of great reputation and merit. As a connoisseur, it is certain that he followed the age-old Byzantine tradition of monumental painting technique, which undoubtedly echoed the common practices of many earlier artists. However, articulating his artistic talent and his creative spirit, he developed his own unique style that strongly affected later icon painters.

Having its centre in Thessaloniki, the Macedonian School flourished in the 13th and 14th centuries. Painters from

Abbreviations: PCA, principal component analysis; SIM, selected ion monitoring; TIC, total ion current; Ala, alanine; Gly, glycine; Val, valine; Leu, leucine; Ile, isoleucine; Ser, serine; Met, methionine; Thr, threonine; Phe, phenylalanine; Asp, aspartic acid; Glu, glutamic acid; Lys, lysine; Tyr, tyrosine; Pro, praline; Hyp, hydroxyproline; Lau, lauric acid; Myr, myristic acid; Palm, palmitic acid; Stea, steatic acid; Ole, oleic acid; Sub, suberic acid; Aze, azelaic acid; Seb, sebacic acid.

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Thessaloniki were invited to paint Athonite foundations and many churches in northern Macedonia, Serbia, Ochrid and Skopia. There were many famous ateliers of the Macedonian School, with the most distinctive ones being the atelier of Manuel Panselinos and that of Michael Astrapas and Eutychios. The painting style of the Macedonian School is mainly characterised of realism in the depiction of the figures, not only in their external features but also in the rendering of their inner world, particularly their pathos. The compositions are crowded, with all the figures moving in the space, which is extensive and rendered in striking depth. The characteristics of the Macedonian School remained apparent in all the wall paintings and portable icons on Mount Athos until the end of the 15th century, when there was a gradual decline in the quality of the painting.

Earlier Protaton investigations (undertaken extensively between 1999 and 2003) on painting techniques and constituent materials of the plaster, the underdrawing, and the stratigraphy of its wall paintings have made possible a complete description of their unique technical qualities possible (Bikiaris et al., 1999; Chiavari et al., 1999; Chryssoulakis and Daniilia, 2005; Daniilia et al., 2000, 2004; Tsakalof et al., 2001, 2003). The present endeavour, however, has two objectives. First, it aims at identifying the organic substances that had been employed as binding media in the paint layers, and secondly, it proposes to classify, in more general terms, the techniques applied by Panselinos to create the wall paintings. An initial impediment to this kind of examination had been the age of the wall paintings; with the passing of so many centuries the composition of the organic substances in the painted layers suffered alteration and deterioration (Colombini et al., 2000; Schilling et al., 1997). Furthermore, the presence of diverse pigments in the samples under inspection and the relatively modest amount of organic substances raised challenges for their identification (White, 1984). Nonetheless, the clear data that has emerged from analyses of samples from the wall paintings, when compared with the evaluation results of the reference samples, have permitted an accurate interpretation of the findings.

The application of diagnostic methodologies for the analysis of the Protaton wall paintings provided scientific data, which could contribute to the development of a proper conservation work. Besides, the results of the study can assist in the rediscovery of lost painting techniques, thereby opening a path to the ''re-creation'' of old masterpieces by the modern icon painters.

The following brief historical survey of the ancient treatises, together with the writings of old and new investigators give valuable information that support the present study regarding the materials used in the Protaton wall paintings.

2. Technological aspects of wall paintings: historic overview

Information about application techniques and materials used in wall paintings from antiquity to the post-Byzantine period can be found in writings by older and contemporary scholars (Cennini, 1960; Dionysios, 1996; Doerner, 1984; Mappae Clavicula, 1974; Mayer, 1991; Pliny, 1977; Theophilus, 1979; Vitruvius, 1999). However, the only clear account specifically concerned with the techniques of Byzantine wall painting is in the eighteenth-century *Painter's Manual* by Dionysios of Fourna (1728–1733). Unfortunately, this treatise contains very few descriptions and these are frequently confusing and of little historic value (Dionysios, 1996). For this reason, treatises on wall painting stemming from other traditions are referred in this study for comparison purposes due to similarities found with the Byzantine painting technique.

2.1. Fresco–secco technique

The institutionalisation of the Italian terms *al fresco* and *al secco* to characterise respectively wet and dry plaster painting has provoked various misinterpretations (Winfield, 1968). The term *al fresco* indicates the technique of painting on damp plaster where a limited number of pigments (chiefly earthy) is mixed simply with water or lime water. On the other hand, *al secco* is used for painting on dry plaster with pigments that are blended with some type of organic binder.

Ancient authors, such as Vitruvius, Pliny and later Lucca and Theophilos, describe in detail the materials and procedures used in preparing plaster for art work (Cennini, 1960; Mappae Clavicula, 1974; Pliny, 1977; Theophilus, 1979; Vitruvius, 1999). They emphasise how important it is to combine the ingredients in a precise sequence in order to ensure endurance and a proper surface for the painting.

In his *Craftsman's Handbook*, Cennini (1960), insisting on the course of action that must be followed in order to prepare plaster correctly, leaves detailed instructions about materials, proportions, layers and how to draw the artistic compositions. The aforementioned Dionysios of Fourna briefly (as he himself admits) describes in his *Manual* the method used by Panselinos in his Protaton wall paintings. As can be surmised from his text, earlier Byzantine painters must also have followed this technique (Dionysios, 1996).

Special attention was given to the preparation of plaster in Byzantine wall painting. The presence of joints in different parts of the plaster, called ''giornata'', testifies clearly at least to the fact that work began wet. In Byzantine wall paintings it is known that such points of connection only occurred either in the decorative frames that surrounded entire iconographic compositions or in the horizontal zones at whose base the scaffolding was mounted (Daniilia et al., 2000). This was very different for instance in Roman paintings or in Renaissance paintings. The frequently encountered practice of joining the plaster where figures are portrayed (and thereby identifying the end point of a working day) is to be found among the Italian masters: rarely can it be seen in wall paintings of the Byzantine period.

Cennini refers to painting on wet plaster, which, owing to the *al fresco* technique's particular demands, is confined to a single day's work, the time normally required for the plaster to dry. He notes, nevertheless, that the completion of a wall painting will inevitably be done on dry plaster, as well (Cennini, 1960).

Even in some sixteenth-century Russian manuals the requirement to finish a wall painting begun on damp plaster and the use of some kind of tempera is affirmed (Dmitriev, 1954). This corroborates the view of recent scholars dealing with Byzantine art that wall paintings began wet but were completed dry with some kind of tempera (Winfield, 1968).

The time taken to work on wet plaster (using water as a medium) is not, however, necessarily confined to that of a single day. Here, one or more important factors must be considered, which include:

- the type, thickness, and dampness of the wall which is to be plastered;
- the materials and thickness of the plaster;
- the season of work and the degree of humidity in the immediate area;
- the ability and speed of the artist;
- the number of artists in the work team.

2.2. The preliminary drawing

The preliminary drawing is a draft underdrawing, which serves as a guide during the subsequent painting process. Depending on the artistic procedure being pursued, one of a number of methods could be employed to render the preliminary drawing onto the plaster. It was Cennini's recommendation that this drawing be first applied quickly to the prime plaster layer with charcoal whereas the final version should be executed by brush onto the plaster's uppermost coat by means of some kind of ochre (yellow or red) mixed with water (Cennini, 1960).

Twentieth-century art research has verified this practice for most Byzantine paintings so far investigated; scholars have located initial drawings sketched both on the first layer of the plaster and on the fine finish, but hardly at all on the edifice's stone wall (Winfield, 1968). The underdrawing was rendered with charcoal or even with ochres diluted in water. Occasionally, the painters used a sharp tool to incise several of the underdrawing lines in the folds of garments. There is again a clear reference in Cennini's treatise to incisions being made by means of a nail or needle to outline the folds of dark garments, which originally had been rendered by brush. In this way these etched drawings remained visible even after subsequent dark colour layers had covered them (Cennini, 1960).

2.3. Binding media and pigments

From the time of Vitruvius and Pliny onwards, wet plaster painting had been prepared using pigments mixed only with water. At the same time, in the case of certain pigments, the same writers refer to the use of organic media, such as glue, gum, egg, honey and milk for binding purposes (Pliny, 1977; Vitruvius, 1999). Theophilos prefers the use of lime as a binding medium; in any case, it was most often lime (kaolin white clay was sometimes used too) that made up the white pigment of the artists' palette (Theophilus, 1979).

An identical scheme is also seen in Cennini's treatise; there he explains how to prepare the lime, which he also declares to be the most appropriate binding medium for painting on wet plaster since it has no need of any other tempera (Cennini, 1960). Continuing this line of thought, Cennini clearly advocates completing on dry plaster the painting already begun on the wet surface and using different binders, such as whole egg, egg yolk, and glue.

Finally, in the account by Dionysios of Fourna (1996) reference is made to the merits of using white lime as a binding medium for painting on wet plaster. As to dry plaster painting, however, Dionysios recommends different binders, such as glue, gum, whole egg, egg white, egg yolk, honey, garlic juice, resin, and wax. This variety most likely refers not only to "Byzantine fresco" but also to techniques and styles, developed in various areas and periods.

Twentieth-century scholars, following detailed macroscopic examinations of wall painting surfaces in many early Christian and Byzantine monuments, have confirmed the use of lime white as the binding medium (Doerner, 1984; Mayer, 1991). Indeed, in certain instances, they also suspected the helpful presence of an organic binding medium (glue, egg, or casein) without having corroborated their conjectures with analytical results (Winfield, 1968). In their opinion, the very best situation for preserving a wall painting, irrespective of the occasionally unfavourable environmental conditions, is when lime white mixed with an organic binding medium acts a binding medium for the pigments.

A recent volume of *Reviews in Conservation* presents the accumulated results of a decade's examination that sought to identify the organic materials used in wall paintings of different countries, cultures and chronological periods (Casadio et al., 2004). In this brief historic overview of the state of research on the ingredients used by Byzantine wall painters for their artistic oeuvre, a great variety of organic materials has been noted: alcohol, whole egg, egg white, egg yolk, casein, animal glue, gum, milk, starch, flour, gall, oil, resin, sugar, varnish, wax and vegetable products. Analyses of unknown samples from a variety of monuments identified whole egg, egg yolk, casein, animal glue, gum, milk, oil, resin, wax. From the inventory of monuments studied using GC/MS, only the Baptistry of Parma, Italy (thirteenth century) belongs to the same period as the wall paintings of the Protaton church. Of interest is the fact that in its wall paintings animal glue and egg were identified as the organic binders for the pigments, since until then it was believed that in "Byzantine fresco" only water was used.

3. Methods

Detection of the preparatory drawing was made possible by infrared reflectography (Van Asperen de Boer, 1970), while the inspection of the cross-sections was completed by means of an optical microscope (10×, 20×, 50×). Thus the structure of the paint layers has been revealed. Inorganic pigments were identified by μRaman spectroscopy and the organic binders were assessed using GC/MS.

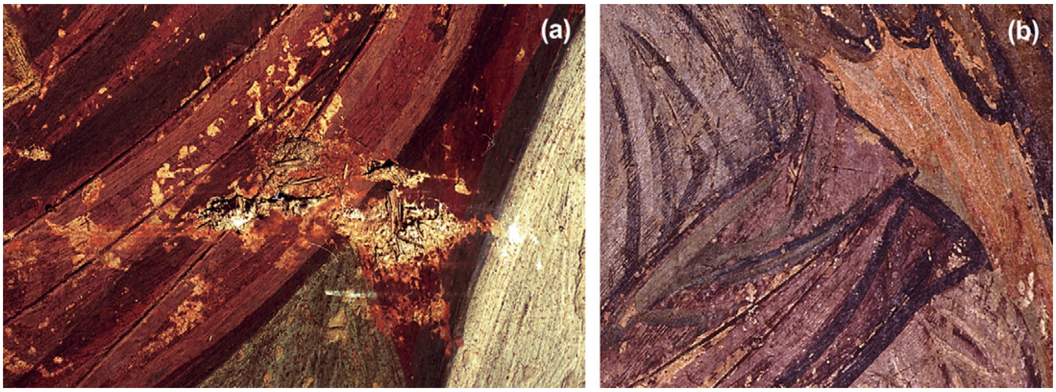

Fig. 1. (a) Photography with raking light. The incised lines of the preliminary drawing are visible. (b) Photography with normal light. A few incised lines have been revealed where the surface paint layers have been detached.

3.1. Infrared reflectography

Infrared reflectograms were taken using a Hamamatsu 2400-03D Precision TV Infrared camera equipped with a Vidicon infrared tube and a Nikon Φ1.2/50 mm lens, in front of which was placed an interference filter at 1800 nm. Image capture and digitisation procedures were controlled through special software (Eikona 1.0).

3.2. Optical microscopy

Samples were mounted in polyester transparent resin so that their cross-sections would provide, after grinding and polishing using a Struers Planopol-V machine, all relevant information from the existing stratigraphy. Cross-sections were observed under a Zeiss Axiotech 100 HD research polarising microscope equipped with a quartz halogen and an ultraviolet excitation light source, an automatic photographic device and a SPOT 2 1.4 digital cooled camera.

3.3. μRaman spectroscopy

The spectra for the identification of the pigments were collected on a Renishaw System 1000 μRaman spectrometer consisting of an Olympus BH-2 imaging microscope, a grating monochromator and a charge-coupled device (CCD) Peltier-cooled detector (576 × 384 pixels). The incident laser excitation was provided by an air-cooled He–Ne laser source, operating at 632.8 nm. The power at the exit of an ×100 objective lens was varied from 1 to 3 mW, depending upon the stability of the pigments identified. Spectra were recorded with a resolution of 4 cm^{-1}, at a collection time of 30 s, and after an accumulation of 10 scans. In order to avoid undesirable Rayleigh scattering, two 100 cm^{-1} notch-filters were employed to cut off the laser line. Pure silicon was used for the calibration of the instrument.

3.4. Gas chromatography–ion trap mass spectrometry (GC/MS)

A Polaris Gas chromatograph–ion trap Mass Spectrometer provided with an AS2000 autosampler (ThermoFinnigan, San Jose, USA) was used for amino acid and fatty acid quantification in reference and real samples. The gas chromatograph was equipped with split/splitless injector and AT™-5MS 30 m × 0.25 mm column with 0.25 μm film thickness of 5% phenyl/95%methylpolysiloxane stationary phase (Alltech Associates, USA).

The analytical procedure is summarised as follows:

- The sample was extracted twice with $CHCl_3$ in order to separate possible natural resins, lipids and free fatty acid from the proteinaceous fraction.
- The solid residue, once dried, was extracted twice with NH_3 2.5 N for 3 h at 60 °C in an ultrasonic bath. The aqueous phase contained the proteinaceous fraction while the residue contained inorganic compounds and part of a lipid fraction, which was not extracted with $CHCl_3$.
- The ammonia solution, once dried, was subjected to acid hydrolysis assisted by microwaves in order to free the amino acids.

Fig. 2. Infrared reflectogram. The preliminary brush drawing has been revealed owing to the minor changes made on the final brushstrokes.

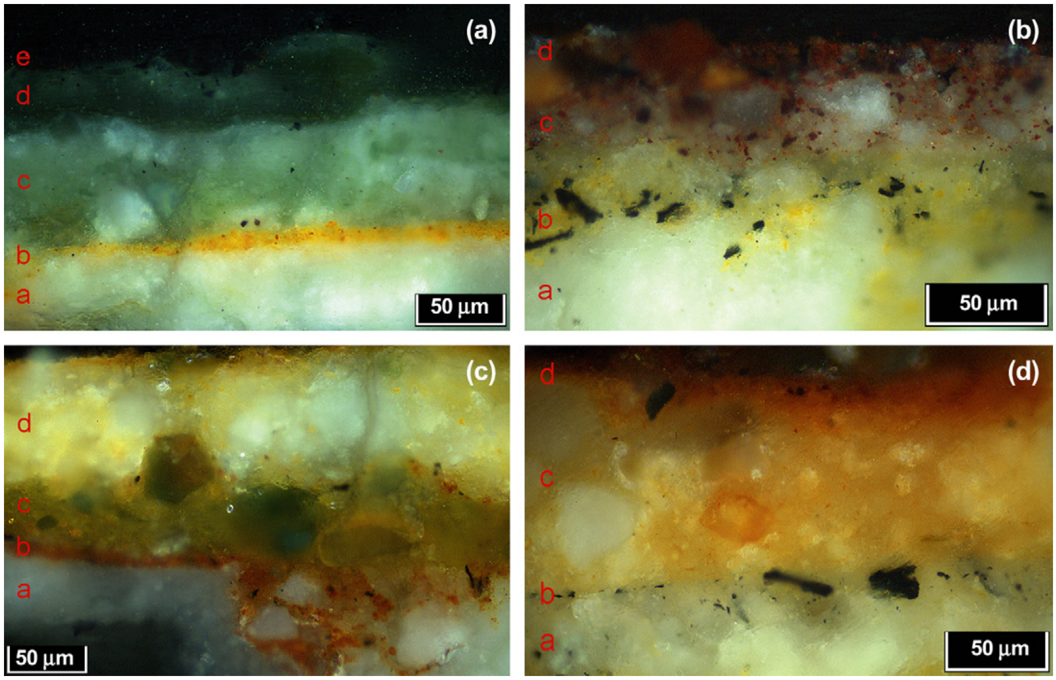

Fig. 3. (a) Cross-section from main line of a green garment: a, lime; b, preliminary drawing: yellow ochre; c, green earth and lime; d, green earth; e, carbon black and green earth. (b) Cross-section from main line of a purple tunic: a, lime; b, preliminary drawing: yellow ochre and carbon black; c, haematite and lime; d, hematite. (c) Cross-section from the flesh tone of a foot: a, lime; b, preliminary drawing: red ochre and carbon black; c, green earth and yellow ochre; d, yellow ochre and lime. (d) Cross-section from main line of orange garment: a, lime; b, preliminary drawing: carbon black; c, warm ochre and lime; d, red ochre. (For interpretation of the reference to colour in figure legends, the reader is refered to the web version of this article).

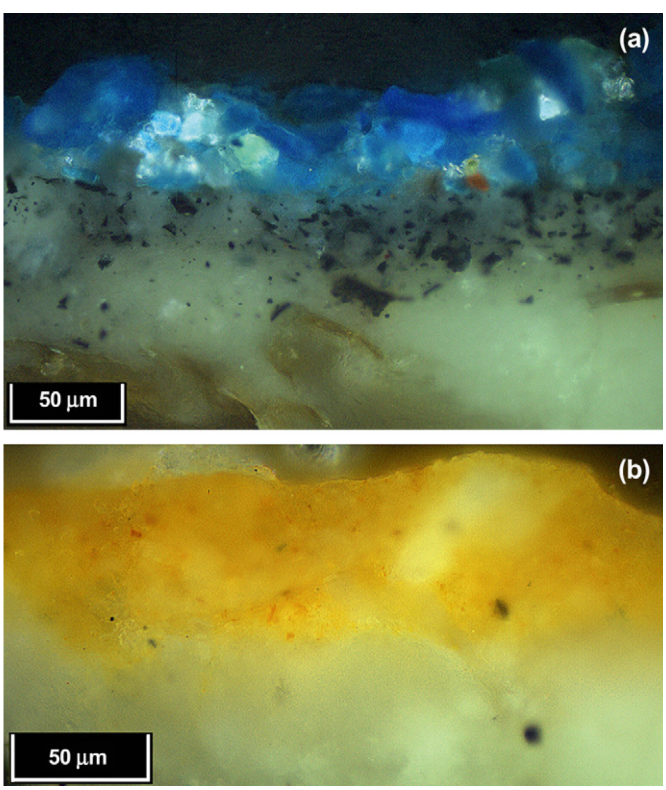

Fig. 4. (a) Cross-section from blue rays on the background of the Baptism. The first grey paint layer has been applied on the wet plaster (intense diffusion). (b) Cross-section from halo. The yellow paint layer has been applied on the wet plaster. (For interpretation of the reference to colour in figure legends, the reader is refered to the web version of this article).

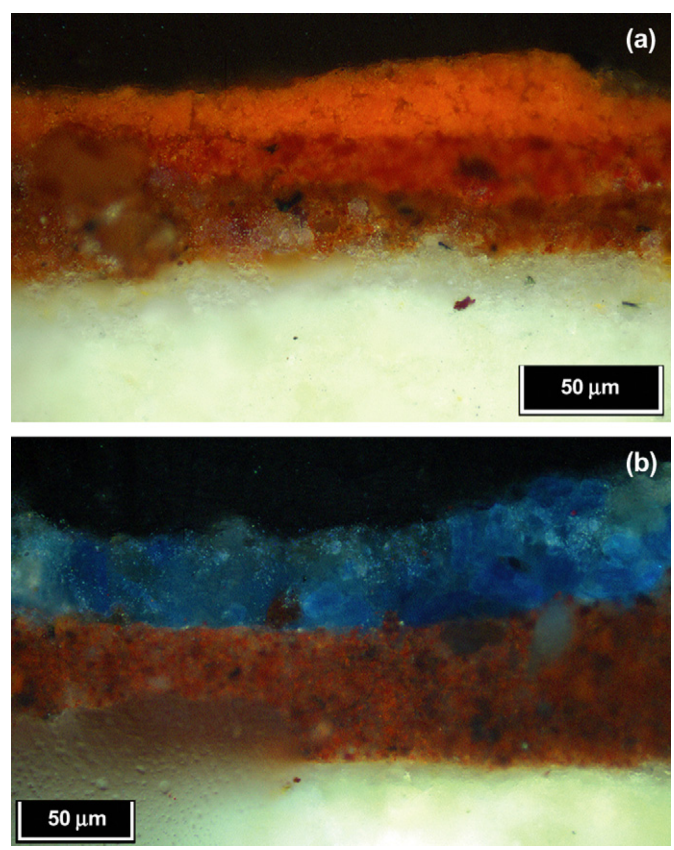

Fig. 5. (a) Cross-section from a red tunic. The three discernible paint layers have been applied with *al secco* technique. (b) Cross-section from Virgin's mantle. The absence of diffusion between the plaster and paint layers imply the application of *al secco* technique. (For interpretation of the reference to colour in figure legends, the reader is refered to the web version of this article).

Fig. 6. (a) The Baptism; (b) The Resurrection; (c) St Theodore the Recruit.

- The $CHCl_3$ extract, which was added to the NH_3 residue, once dried, was subjected to saponification with aqueous KOH in order to free the fatty acid.
- Both amino acids and fatty acids were derivatised with N-*tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide and then 1 μl (of each derivatised solution) was analysed by GC/MS in two separate analytical procedures.

These procedures allowed for the determination of 15 amino acids and eight fatty acids.

Application of principal component analysis (PCA) to the amino acid percentage content of the real samples allowed identifying the proteinaceous binder.

4. Results and discussion

Before drawing conclusions about the techniques used in the wall paintings of the Protaton church, it was necessary to examine the materials and the technical application of the plaster, the preliminary drawing, and the painting's entire stratigraphy. There followed in turn the identification by means of GC/MS technique of the organic binding media in the paint layers.

4.1. The plaster

The fine outer plaster (1 mm thick), consisting solely of lime diligently levelled out, offers an even and lustrous surface for the painting. The underlying plaster (up to 3 cm thick) is composed of straw and lime (with added ingredients of quartz [SiO_2] and albite [$NaAlSi_3O_8$]). The presence of an ample quantity of straw in this plaster guaranteed a lengthier period of humidity preservation for the wet plaster (Cennini, 1960; Dionysios, 1996; Thompson, 1956; Winfield, 1968).

Aside from the points separating the four horizontal zones in the iconographic programme, no other signs of connection

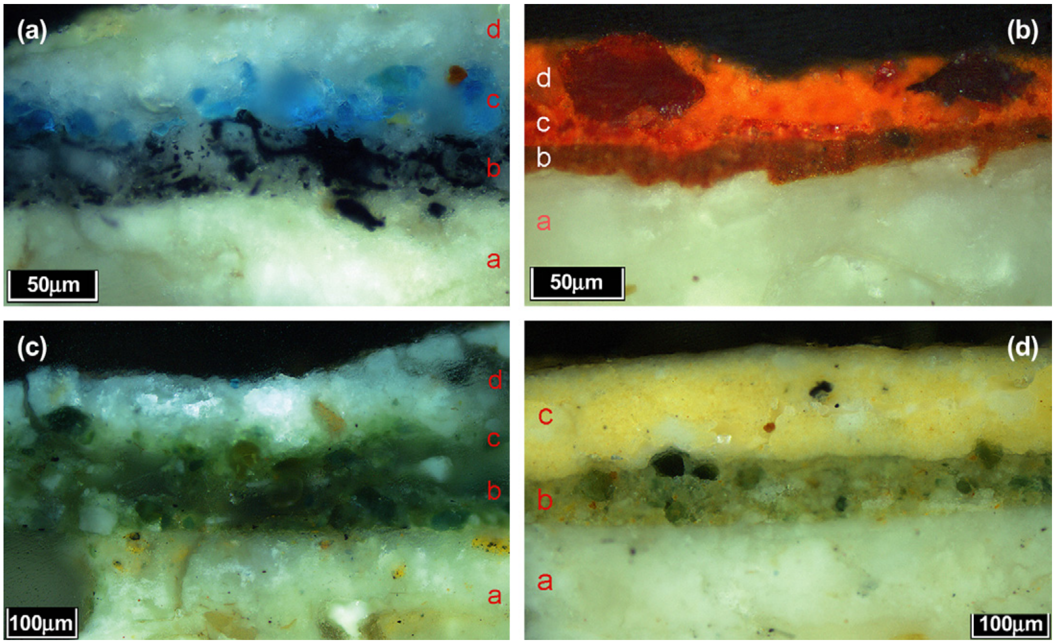

Fig. 7. (a) Cross-section from an inscription (sample P8, Table 1): a, lime; b, carbon black and lime; c, azurite; d, lime. (b) Cross-section from highlight of a red tunic (sample P6, Table 1): a, lime; b, red ochre; c, cinnabar; d, minium. (c) Cross-section from highlight of a green tunic (sample P5, Table 1): a, lime; b, green earth and grains of lime; c, lime and green earth; d, lime. (d) Cross-section from flesh tone of a hand (sample P3, Table 1): a, lime; b, green earth, yellow ochre and lime; c, yellow ochre and lime. (For interpretation of the reference to colour in figure legends, the reader is refered to the web version of this article).

in the final plaster were detected. Even in large-scale scenes such as the Dormition of the Mother of God (2 × 7 m), which completely occupies the second zone of the Church's west wall, there are no discernible intervening vertical joints. It would indeed be impossible to imagine—even assuming the involvement of many experienced artists pursuing a systematically organised work schedule—that over such a large surface area the *al fresco* technique (with water or limewater as binding medium) would have continued unceasingly to the final stage of the painting.

4.2. The preliminary drawing

Raking light ascertained the existence of scattered drawing incisions in certain areas of the garments (Fig. 1a). At points where the overlying paint layers had peeled off, it was possible to distinguish clearly the underlying scoring, which, incidentally, the artist did not always follow with accuracy in his final brush strokes of the dark lines (Fig. 1b).

The preliminary brushwork was detected initially with infrared reflectography at points where the final dark lines did not follow the underdrawing precisely (Fig. 2). On close examination of the cross-sections, the use of a variety of colour combinations in the brushwork could be established. While the choice of pigments was connected with the shade, which the

Table 1
Sampling

Sample	Sampling position
P1	Face of St Artemius: warm flesh tone (Zone 1)
P2	St Artemius: hair highlight (Zone 1)
P3	St Theodore the Recruit: flesh tones of hand (Zone 1)
P4	Baptism: purple highlight of angel's cloak (Zone 2)
P5	Resurrection: green highlight of Solomon's tunic (Zone 2)
P6	Maiden in Entry scene: red highlight of tunic (Zone 2)
P7	Maiden in Entry scene: greenish flesh tone of hand (Zone 2)
P8	St Mercurius: letter from inscription (Zone 1)

Table 2
Mean values of the relative percentage content of amino acids in reference samples

Amino acids	Egg		Casein		Glue	
	$\bar{x}^{a}$	SD	$\bar{x}^{b}$	SD	$\bar{x}^{c}$	SD
Ala	7.8	0.7	4.8	0.6	10.7	1.1
Gly	4.8	0.3	3.7	0.7	22.9	4.5
Val	3.7	0.6	4.1	0.4	1.4	0.6
Leu	9.9	0.9	8.4	0.9	3.6	1.1
Ile	2.7	0.3	3.2	0.4	0.9	0.3
Met	2.3	0.3	3.9	0.9	0.8	0.7
Ser	10.2	0.6	5.6	1.0	4.6	0.8
Thr	4.3	0.6	3.9	0.6	2.2	0.5
Pro	4.1	0.8	10.3	1.6	11.4	1.7
Phe	4.0	0.3	5.8	0.6	2.1	0.6
Asp	12.5	0.5	7.4	1.3	5.7	0.5
Glu	16.2	1.8	18.8	2.5	11.3	1.5
Lys	12.8	4.2	12.7	3.5	8.3	4.0
Hyp	0.0	0.0	0.0	0.0	13.6	2.9
Tyr	4.6	0.9	7.5	0.9	0.4	0.2

[a] Average from 7 reference samples.
[b] Average from 10 reference samples.
[c] Average from 10 reference samples.

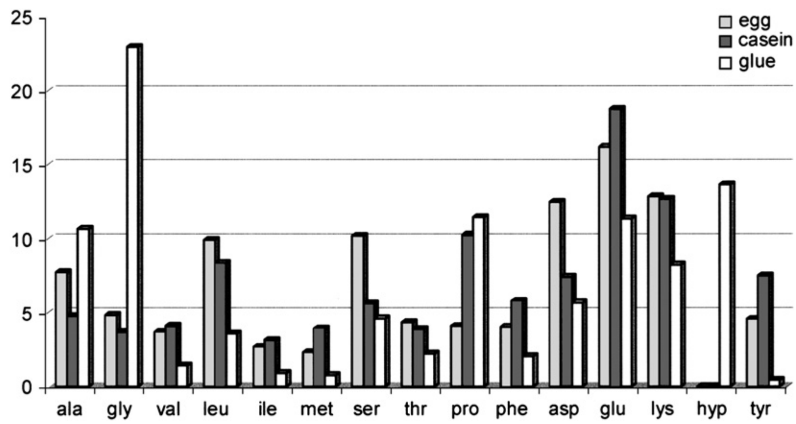

Fig. 8. Histogram of mean values of the relative percentage content of amino acid in reference samples.

colour area would later cover, it did not appear, however, that any fixed rules were necessarily being followed. Yellow ochre was used in the drawing of the green garments (Fig. 3a), a mixture of yellow ochre and carbon black for the purple garments (Fig. 3b), a mix of red ochre and carbon black for the lines of the faces, hands and feet (Fig. 3c) and, more rarely, pure carbon black, as seen, for example, in the orange garments (Fig. 3d).

Thus, the preparatory drawing was rendered with a brush and diluted water colour over wet plaster. In certain instances the lines of the folds were later incised with a sharp tool so that they would remain visible even after they had being covered by dark paint layers.

4.3. Pigments and paint techniques

The number of pigments used is exceptionally limited: lime white or calcite ($CaCO_3$), carbon black (C), yellow ochre ($Fe_2O_3 \cdot H_2O$ silica and clay), orange ochre ($Fe_2O_3 \cdot H_2O$ and Fe_2O_3), red ochre (Fe_2O_3 clay and silica), haematite (Fe_2O_3), green earth (hydrous iron, magnesium and aluminium potassium silicate), mineral cinnabar (HgS), minium (Pb_3O_4) and azurite ($2CuCO_3 \cdot Cu[OH]_2$). Most of them are earthy, suitable for painting on wet plaster. The lime white (or calcite) constitutes the only white pigment in the Protaton wall paintings. It was used sparingly in the first paint layers (most likely in the form of limewater) whereas it constitutes the chief

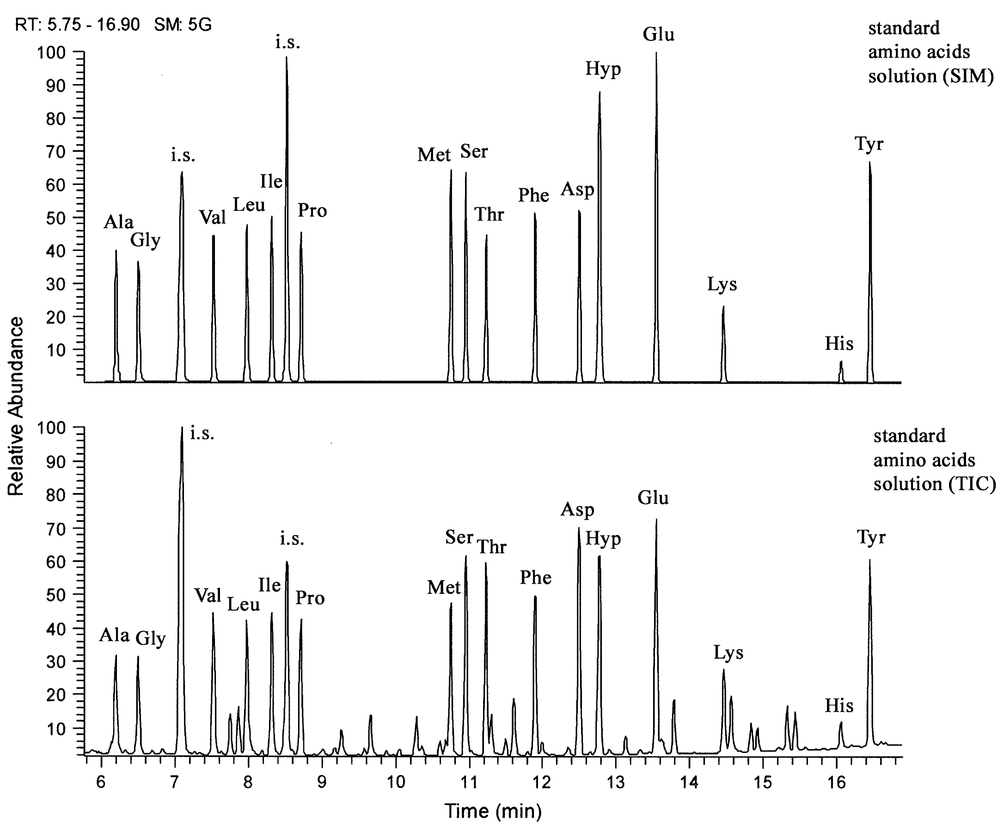

Fig. 9. Representative chromatogram of amino acid standard solution acquired in SIM and TIC modes of MSD.

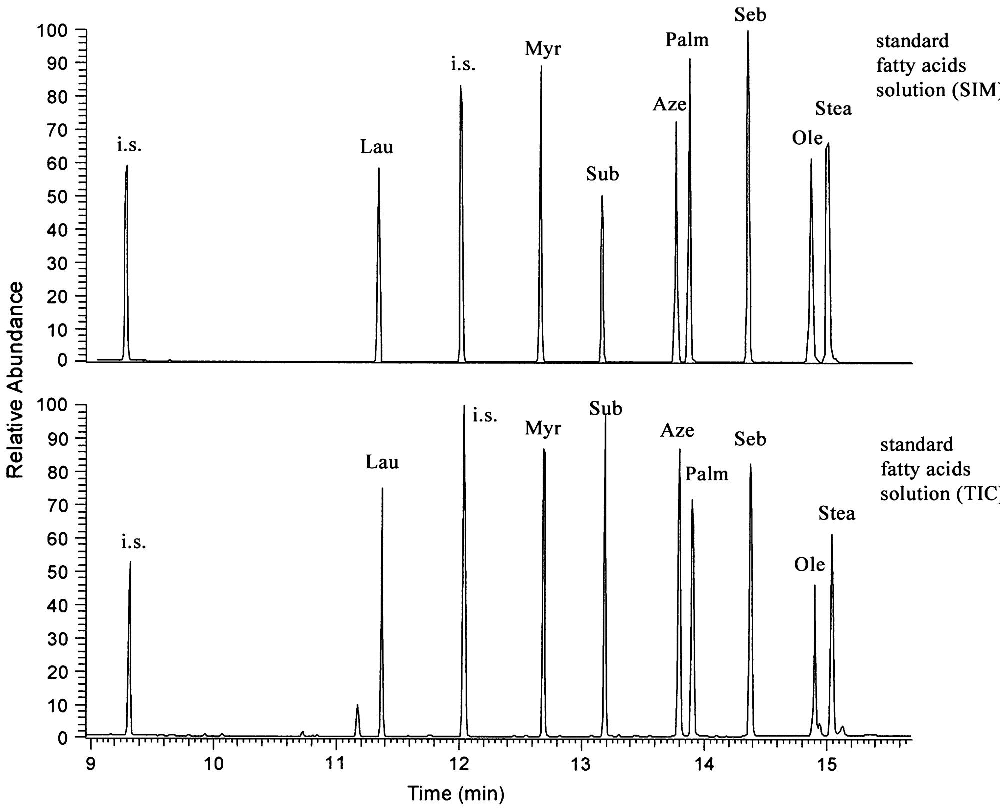

Fig. 10. Representative chromatogram of fatty acid standard solution acquired in SIM and TIC modes of MSD.

component in the gradations of the highlights. With the exception of the ochres—which comprise the basic pigments in the palette and can be used on wet plaster—azurite, cinnabar and minium tend not to be preferred for *al fresco* technique (Casadio et al., 2004; Cennini, 1960; Fitzhugh, 1986; Thompson, 1956). These sources offer directions for the latters' use, facilitated by some binding medium (animal glue or egg), on dry plaster.

Additional meticulous microscopic study of the cross-sections in a representative number of samples have confirmed that there were differing degrees of diffusion between the first paint layer and the white plaster found immediately below it. Pigments of similar grain size (such as ochres, haematite, etc.) used in various painting areas were found to diffuse into the plaster to a different degree (Figs. 4b and 5a,b). For instance, on the grey background and in the yellow ochre of the halos (Fig. 4) as well as in the preliminary brush drawing (Fig. 3) an intense diffusion of the pigment moving into the white plaster can be observed, indicating the application on wet plaster. However, in the majority of cases, the separation line between the plaster and the first as well as the overlying paint layers are especially distinct, by virtue of their application on dry plaster. This phenomenon has been observed in many colour combinations and especially in the red garments, whose highlights used cinnabar and minium (Fig. 5a), and in those purple garments with highlights in azurite (Fig. 5b). It is noteworthy that even when the highlights are executed in lime white, such as in the painting of the faces (Fig. 7d), the absence of diffusion is frequently observed—a fact that testifies to painting on dry plaster with the use of some kind of organic binding medium.

Table 3
Relative percentage content of amino acids in the Protaton samples

Sample	Ala	Gly	Val	Leu	Ile	Met	Ser	Thr	Pro	Phe	Asp	Glu	Lys	Hyp	Tyr
P1	5.6	16.2	5.4	7.8	3.6	0.0	11.1	2.7	3.8	3.6	17.9	21.6	0.0	0.8	0.0
P2	8.0	18.3	3.7	6.4	2.6	0.0	11.2	2.3	4.0	3.3	15.9	19.0	2.5	0.6	2.0
P3	7.3	9.4	7.9	14.1	6.7	0.0	4.6	0.6	13.3	2.4	12.3	17.5	1.4	1.4	1.1
P4	9.3	10.9	7.7	9.3	6.2	0.2	5.9	2.2	6.1	3.4	16.4	19.2	0.6	2.0	0.6
P5	7.4	10.2	5.1	7.9	3.9	0.0	9.9	3.4	4.6	3.4	18.6	24.2	0.9	0.4	0.1
P6	8.1	11.2	5.5	7.6	3.4	0.0	7.8	3.5	6.1	3.4	15.5	24.7	1.1	1.6	0.4
P7	9.3	12.0	6.2	6.1	3.8	0.0	5.2	1.6	6.3	2.4	18.9	23.0	3.1	1.7	0.3
P8	11.4	16.8	3.9	9.3	2.2	0.0	12.8	1.8	1.7	3.8	14.1	16.7	3.5	0.9	1.1

4.4. Binding media

Recent publications have presented the results achieved by employing analytical methods both to identify organic materials in works of art and to measure the effect of ageing of those materials in their identification (Colombini et al., 1995, 1998a,b, 1999; Rampazzi et al., 2002).

With the application of GC/MS, the organic media of eight samples from the Protaton (Table 1) could be identified. These samples, originating from six different scenes belonging to different zones and areas of the church (Fig. 6), are representative of the monument's entire painting programme, which covers a wide range of colour combinations. As a result it is possible to perform a comparative study with respect to the entire technique applied. Samples were examined from the background, the inscriptions, the red, purple, and yellow garments, as well as from faces, hands and hair (Fig. 7).

It is of value to be reminded that the chief characteristic of Byzantine wall painting is the superimposition of paint layers. For this reason, all intervening paint layers of the Protaton samples have been identified in the cross-sections, from the plaster to the surface. The Byzantine artists aimed at clear drawing and simple, distinct tonal gradations, since this contributed to the spiritual message that is represented by a religious image.

In order to study the results of GC/MS it was first necessary to analyse the reference substances of the egg, animal glue and casein (Table 2, Figs. 8–10) and then to compare the results with data from the unknown Protaton samples (Tables 3 and 6, Figs. 11–13). Recognition of the nature of the protein binding medium was effected by a quantitative determination of both amino and fatty acids; their characteristic ratios were examined (Tables 4–6) and the principal component analysis (PCA) in the percentage content of the amino acids was applied (Figs. 14 and 15).

Table 3 summarises the protein content, which fluctuated between 0.05% and 0.29% (w/w). The Protaton samples contain amino acids whose characteristic ratios concur with those of egg (see the figures derived from a comparison of the Protaton samples with the reference samples of egg, casein and animal glue [Table 5]) (Casoli et al., 1998; Colombini et al., 1995, 1998a). The small differentiations, noticeable when comparing the Protaton samples with the reference samples of egg and the inorganic pigments, are most probably due to the presence of inorganic pigments in the former (Colombini et al., 1995, 1998b, 1999b; Halpine, 1992). The identification of hydroxyproline (Hyp) in the Protaton samples (Table 3) indicates the presence of a small quantity of animal glue (0.4–1.2%) (Casoli et al., 1996; Halpine, 1992). Minor amounts of the amino acids tyrosine (Tyr) and lysine (Lys) are the result of the egg's ageing process (Karpowicz, 1981).

Table 4
Amino acid concentration ratios in the Protaton samples

Sample	Gly/Glu	Gly/Asp	Pro/Asp	Glu/Pro
P1	0.7	0.9	0.2	5.7
P2	1.0	1.2	0.3	4.8
P3	0.5	0.8	1.1	1.3
P4	0.6	0.7	0.4	3.2
P5	0.4	0.5	0.2	5.3
P6	0.5	0.7	0.4	4.0
P7	0.5	0.6	0.3	3.6
P8	1.0	1.2	0.1	10.0
$\bar{x}$	0.7	0.8	0.4	4.7
SD	0.2	0.2	0.3	2.5

Table 5
Amino acid concentration ratios of the reference samples (egg, casein, glue); Protaton samples and samples with egg containing pigments

Amino acids ratios	Egg	Casein	Glue	Protaton samples	Egg and pigments
Gly/Glu	0.3	0.2	2.0	0.7	0.5
Gly/Asp	0.4	0.5	4.1	0.8	0.7
Pro/Asp	0.3	1.4	2.0	0.4	0.4
Glu/Pro	4.0	1.9	1.0	4.7	3.6

Table 6 notes the quantities of fatty acids and their characteristic ratios in eight samples from the Protaton. To identify the binding medium, the ratios azelaic acid/palmitic acid (A/P) and palmitic acid/steatic acid (P/S) and the sum of the dicarboxylic acids SD% were examined. To the fatty acids of the reference egg belong the values: $A/P < 0.1$, $P/S = 2.3–3$ (Casoli et al., 1998; Colombini et al., 1999a; Mills and Withe, 1994; Schilling et al., 1997) and $SD\% < 1.5$ (Colombini et al., 1999a). For the Protaton samples the low value of the ratio A/P indicates the use of egg yolk while the small increase observable in several samples (0.2 and 0.3) is due to the ageing to which they have been subjected (Colombini et al., 2000). The increase of the dicarboxylic acids SD% (7.7–18.6) and the low values of the ratio oleic acid/steatic acid (O/S) (0.2–0.9) are due to the oxidisation of the polyunsaturated fatty acids of the egg (Casoli et al., 1998; Mills, 1966; Mills and Withe, 1994; Schilling et al., 1997). The chromatogram of Fig. 13 also traced peaks of lower carbon chain dicarboxylic acids (malonic, succinic, glutaric, adipic and pimelic acids)—owing to the oxidisation of polyunsaturated fatty acids (Colombini et al., 2002).

A final observation of the analytical results was based on the application of PCA to the relative percentage of the amino acids in the samples and in the reference materials (egg, animal glue, casein) (Colombini et al., 1998b, 1999a; Colombini and Modugno, 2004; Lletí et al., 2003; Rampazzi et al., 2002). It ought to be mentioned here that the PCA method cannot be used to identify fatty acids because, over time, the amount of dicarboxylic acids significantly increased and the unsaturated acids practically disappeared. The result is that the aged samples do not correspond with the cluster of the reference egg (Colombini et al., 1999a).

In the PCA score plot of the relative percentage amino acids, the Protaton samples are found nearest to the cluster of pure egg (Fig. 14). An observable, slight tendency towards the cluster of animal glue is probably due both to the detection of a little glue in the Protaton samples (Table 3) (Tsakalof et al., 2003), and to the influence of the inorganic pigment

Table 6
Relative fatty acid percentage content, fatty acid ratios and the sum of dicarboxylic acid relative percentages in the Protaton samples

Sample	Lau	Myr	Sub	Aze	Palm	Seb	Ole	Stea	A/P	P/S	O/S	∑D %
P1	1.2	10.1	2.2	5.1	50.4	0.3	11.4	19.2	0.1	2.6	0.6	7.7
P2	1.7	11.5	3.1	5.4	54.3	0.5	6.9	16.5	0.1	3.3	0.4	8.9
P3	1.4	12.4	3.2	6.3	52.9	0.7	10.5	12.5	0.1	4.2	0.8	10.3
P4	1.9	12.1	3.0	7.3	47.8	0.5	11.8	15.6	0.2	3.1	0.8	10.8
P5	2.1	10.9	2.8	6.2	51.4	1.4	5.5	19.7	0.1	2.6	0.3	10.4
P6	1.1	10.9	3.0	6.4	53.4	0.4	11.8	13.1	0.1	4.1	0.9	9.8
P7	2.0	12.3	5.1	12.4	42.7	1.1	11.4	13.0	0.3	3.3	0.9	18.6
P8	2.0	8.0	5.0	9.5	63.5	0.7	2.0	9.3	0.1	6.9	0.2	15.2

content in the samples. Study of this influence in the observed shift of the Protaton samples from the cluster of pure egg, was achieved by examining a few reference samples prepared with egg and different inorganic pigments. In the new PCA score plot (Fig. 15) the Protaton samples are found to be nearer to the cluster of egg-pigments. Colombini et al. (2000) have demonstrated that artificial ageing (UV light at 254 nm or 366 nm at 20 °C and 80% RH) does not significantly affect the amino acid profile of protein binders and consequently, protein binders in old paintings can be reliably identified by comparing the amino acid composition with that of reference paint materials which have not been aged. The same conclusion was made by Tsakalof et al. (2004) concerning biological ageing, growth of the fungus *Aspergillus niger*, of animal glue. Finally, apart from the inorganic pigments, the shift can also be attributed to the natural ageing both of the egg protein and of the animal glue (Rampazzi et al., 2002), given that the Church's wall paintings were completed at the end of the thirteenth century.

5. Conclusions

The techniques employed in the wall paintings of the Protaton Church on Mount Athos can be considered representative of a legacy that has been handed down for hundreds of years and today is known as the "Byzantine fresco". We believe that the conclusions presented in this study comprise a notable guide for contemporary artists who wish to continue painting in the Byzantine style. At the same time they contribute to the genuine conservation of this most noteworthy late thirteenth-century monument of the Macedonian school. The procedures and the materials used for the plastering (particularly the large quantity of straw), the presence of joints in the plaster at the horizontal zones of the iconographic

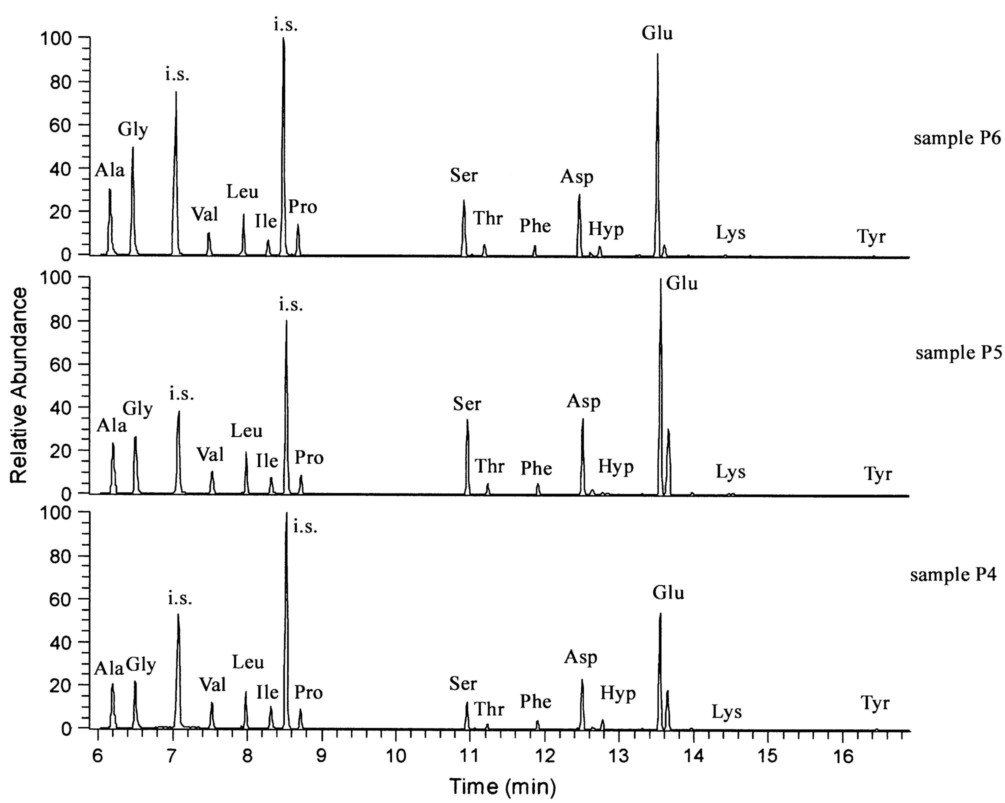

Fig. 11. Chromatogram of amino acids of the samples P4, P5 and P6 in SIM mode.

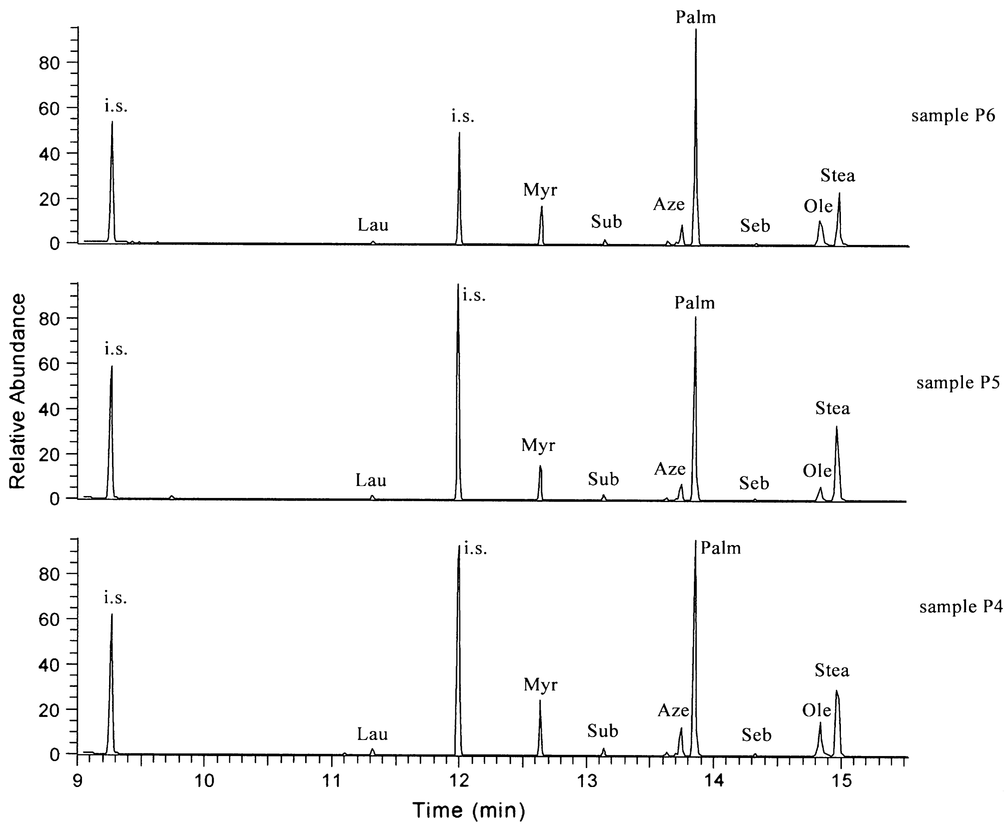

Fig. 12. Chromatogram of fatty acids of the samples P4, P5 and P6 in SIM mode.

programme and the detection of underdrawing incisions offer clear evidence that the art work began its life on wet plaster.

Panselinos' palette includes both earthy and mineral pigments, suitable for painting on wet plaster. The exceptions are azurite, cinnabar and minium, which alone are applied by an organic binder, on dry plaster. Differentiations in the degree of diffusion of the colour layers in the underlying plaster indicate painting sometimes on wet and sometimes on dry

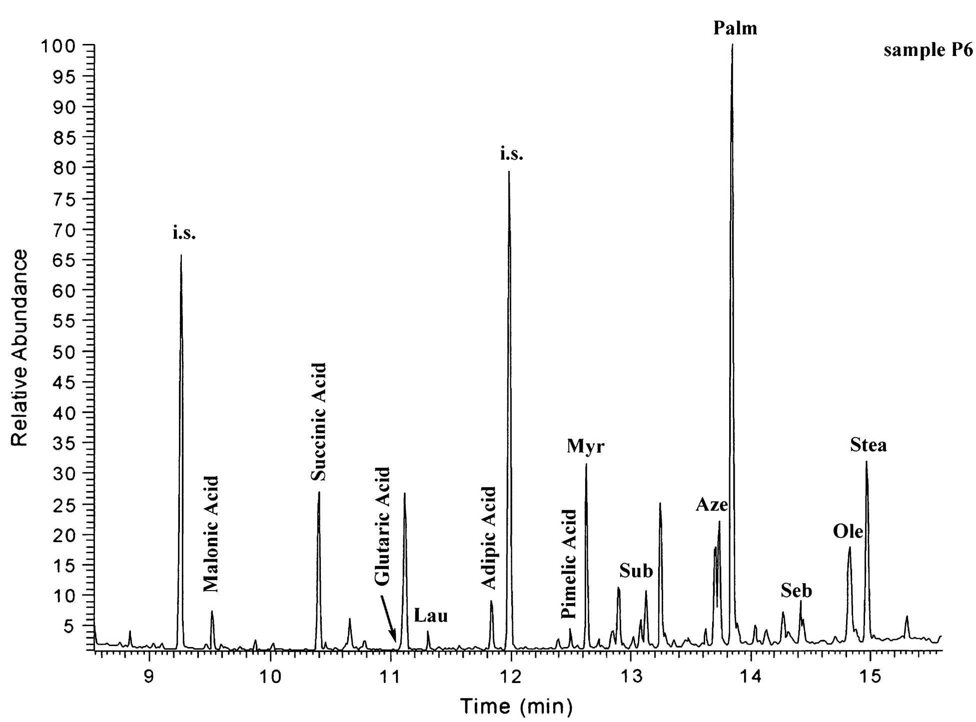

Fig. 13. Total ion current chromatogram of fatty acids of P6 sample.

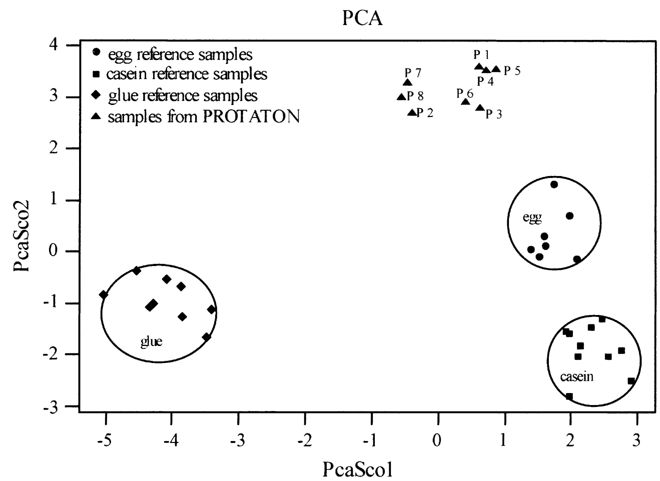

Fig. 14. Principal component analysis (PCA) of amino acid percentage data of reference samples (egg, animal glue, casein) and wall painting samples from the Protaton Church, Mount Athos.

plaster. Moreover, the use of limewater in the initial paint layers, and more generally of lime (or calcite) as a white pigment and a binding medium, assured admirable resistance and stability for the paint layers of the wall paintings.

In each of the analysed samples, which originate from different areas of the edifice and encompass a variety of compositions, pigments and colour combinations, egg yolk and a small amount of animal glue could be detected. The combined use of inorganic pigments, lime white and organic binders impose an excellent mechanism of stabilisation of the paint layers creating complex organic compounds. The most significant agent that has preserved the wall paintings in excellent condition (in spite of the most adverse environmental conditions and the diversity of later interventions with the attempts to restore the edifice) was the addition of a protein binder to the paint layers.

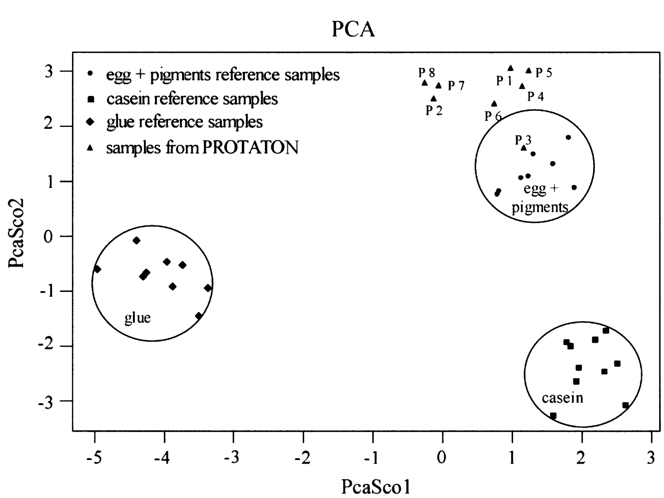

Fig. 15. Principal component analysis (PCA) of amino acid percentage data of reference samples (egg with pigments, animal glue, casein) and wall painting samples from the Protaton Church, Mount Athos.

In giving an account of the “Byzantine fresco”, at least on the basis of the Protaton wall paintings, our reference is to a supple technique, independent of the temporal limitations of pure *al fresco*. The painting, initiated on wet plaster with simultaneous use of limewater and egg/animal glue, was finished on dry plaster with lime white and the same organic binding medium.

Thus by exploiting contemporary analytical methods it has become possible to trace step by step the techniques employed in Byzantine iconographic and monumental painting from an authentic perspective. Empirically based scientific study has revealed in meticulous detail the lost traditions of Byzantine art: one of the unique treasures of the world’s cultural heritage. Not only this, scientific analysis has also facilitated this art’s reading, understanding and continuity into the future.

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