"THE CORONATION OF THE VIRGIN" A NEW ACQUISITION OF THE HOLLY MONASTERY OF ST JOHN THEOLOGOS OF PATMOS: PHYSICOCHEMICAL RESEARCH & CONSERVATION TREATMENT OF THE ARTEFACT

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Keywords
Panel paintings, Binding media identification, Egg tempera, Ethyl chloroformate derivatives, Gas Chromatography

1. Introduction

Byzantine art and the consequent artistic styles have been thoroughly studied so far. They have been studied in terms of history and art. However, no extensive scientific research has taken place as far as the physicochemical study of those artifacts is concerned. Thus, the characterization and identification of the constituent materials of an icon is something relatively new.

The basic structure of a panel painting [1] comprises the substrate, the gesso ground, the paint layers, and the varnish. The paint layers consist of inorganic or organic pigments and the binding medium. The role of the binder is to keep the grains of the pigment together and to hold the paint onto the ground layer.

Physicochemical methods are able to characterise those materials. However, even though the identification of the pigments is a relatively easy process, the determination of the organic binding media is quite problematic [2-5]. Analytical methods such as gas chromatography [6-8], gas chromatography combined with mass spectrometry (GC-MS) [9-11] and high performance liquid chromatography (HPLC) [12] are used for the determination of the organic binders. The proteinaceous binding media are identified on the basis of the relative abundance of some amino acids, as obtained by measuring the relevant peak areas. Each proteinaceous material has a distinct amino acid composition [13-15]. The gas chromatographic analysis of the fatty and dicarboxylic acids content in binding media has been used to identify egg tempera and emulsions of proteins with drying oils [16].

However, there are other non-destructive methods, which in combination, can contribute to the characterization of the binding media: Energy Dispersive X-ray Analysis and Fourier Transform Infrared Spectroscopy (FT-IR) [17-22].

"The Coronation of the Virgin", a 15th century panel painting, is the latest acquisition that was added to the Holly Monastery of St Ioannis of Theologos of Patmos' collection in 2004. Before treating the artefact, physicochemical study took place in order to provide the necessary information about the materials and the construction technique. This information was used for the determination of the conservation scheme that would be followed.

The current paper is focused on (i) the determination of the pigment and binding medium of the paint layer by following a protocol that allows the full exploitation of the sample and (ii) use of the results in order to choose the proper method of treatment.

2. Historical Background

The fall of the Byzantine Empire in 1453 marks the beginning of one of the most important periods of the Greek history of art [23]. The Post-Byzantine era, which lasted until the establishment of the first Greek State, was the transitional period where the art of panel painting through strong interchanges with the western world, changes gradually style; from religious to civil. At the same time, the artists' technique evolves; the painter changes the means of creation and from egg tempera on wooden panel, oil painting on canvas is introduced. Cultural influences also brought a change in the iconographic types: the artist exempts himself from the strict Byzantine rules of depiction in order to acquire the right of free expression [24-25].

2.1. The Coronation of the Virgin

In 2004, a private collector donated the icon "The Coronation of the Virgin" (Fig.1) to the Holly Monastery of St Ioannis of Theologos of Patmos. The Icon according to the epigraph and the records was manufactured in 1474 possibly by a Venetian artist. The subject of this painting does not belong to the typical Byzantine thematology, while the iconographic types follow the basic principles of Renaissance Painting.

Comparing this icon with a typical Byzantine Virgin Mary Hodegetria (Fig. 2), one could easily discriminate the approach of the artist. The western type is being represented with brilliant colours and naturalistic forms. The Mother and Child are being depicted with gay colours, detailed attribution of the clothes and intent gaze and attitude.
On the contrary, the Byzantine type is austere and monumental. The drawing and the colours are strict and specific, while the artist acts as the means of God's expression.

The Icon was painted on a carved wooden panel on gesso ground and on the reverse side of the painting, there is a metal plate. The artefact was not in a good condition. The substrate, which consists of two pieces of wood binded with butterfly joints, was seriously infected by wooden boring insects, leading thus to an alteration of the mechanical properties, while it presented warping. There were traces of use of a frame nailed on the front surface.
Generally, the painting presented loss, cracking and detachment of the paint and the gesso preparation layer.

The overall condition created a series of questions concerning its preservation and exhibition.

Figure 2: *"Virgin Mary, the Hodegetria (She who leads the way)"*

3. Physicochemical Research

3.1. Experimental Procedure

The techniques and the materials used by the artists are directly affiliated with the Icons have been the subject of very little research, possibly due to the complexity of materials used. While the analysis of the inorganic components has acquired a nearly routine character, the identification of the organic media still encounters severe difficulties [26].

Taking a sample from a panel painting is a problem, since it affects the integrity of the artefact. Usually, the quantity required is around 1 to 2 mgs and this should come only from the paint layer, in the form of powder. Therefore, a methodology had to be set up in order to ensure two things:

1st - As much information as possible would definitely be obtained from each sample, and

2nd – The analysis of the samples should start by using non-destructive methods for obtaining a first set of results before proceeding to a destructive method such as GC, which appears to be necessary for the positive identification of egg and drying oil, but with which there is always a risk of loosing the sample.

Taking into consideration the above-mentioned factors, the following methods were chosen:

- Energy dispersive X-ray analysis for the detection and gross identification of the pigments present;
- Fourier transform infrared microscopy for pigment identification and detection of the amide linkages for egg, and the triglycerides for the oils;
- Gas chromatography for medium identification and verification of the results obtained by micro-FTIR.

Artificial standards by following the traditional recipes of both Byzantine [27-28] and western techniques [29] were created and then aged [30], in order to be able to compare them with original samples and create a database for FTIR and GC.

The binding media chosen were: pure organic media (egg yolk, linseed oil, poppy oil, walnut oil, animal glue, casein) and emulsions (egg yolk – linseed oil, egg yolk – poppy oil and egg yolk – walnut oil).

The pigments were: cinnabar, red lead and lead white. The choice of those pigments was based on the fact that they were typical pigments of the artist's palette and that they are of inorganic origin fact that would ease the methodology.

3.2. Sample Collection

The samples from the icon were taken under the microscope, after the surface of the icon had been examined thoroughly for previous

treatments and alterations. The varnish was removed with a suitable solvent, the paint layer was scraped carefully not to remove part of the preparation layer with a scalpel and the powdered sample was placed into a sample vial. The weight of the sample was 0.5 –1mg.

3.3. Experimental Procedure

3.3.1. Determination of Pigments using SEM-EDX

Each of the samples was mounted on aluminium stubs using a black double-side tape, which contained a conductive adhesive. Since all the samples contained inorganic pigments, coating was not necessary.

The instrument used for the analysis was an SEM-EDX Leica S430 with an Oxford ISIS 200 EDX. The acceleration voltage used was 20 kV and the probe current was 600 pico-Amperes. The instrument was calibrated before the analysis of the samples.

Analytical procedure

Each sample was analysed twice, in two different areas of its surface, to minimise the percentage of error. Image from the SEM, X-ray spectra and quantitative charts from the EDX were obtained for each sample. EDX analysis gives elemental information on the constituency of a sample. Since it is not a purely quantitative method, two areas of each sample had to be analysed in order to obtain some quantification, which if it could not be considered as representative of the sample tested, it would at least be indicative of the amounts of elements present.

3.3.2. Determination of Pigments & Binding Media using micro-FTIR

A minute quantity of each sample was placed in a compression cell between diamond windows. The sample was, then, placed under the microscope, the background was ran and subtracted and then the sample was run to record its spectrum.

The instrument to be used was a Nicolet 5DXC FTIR Spectrometer coupled to a SpectraTech IR-PLAN^{TM} Infrared Microscope Accessory and a MTC (Mercury Cadmium Telluride) detector filled in with liquid nitrogen. The analysis was carried out in transmittance mode. The spectra were recorded after 128 scans, with a resolution of 8 cm^{-1}. The spectra obtained were from the mid-infrared region of 4000 to 650 cm^{-1}. The aperture below and above the sample is 100 microns wide to 50 microns long.

Analytical procedure

Two samples were analysed from each sample, in order to ensure that good quality results, minimisation of error and most importantly all the peaks have been recorded. Each sample was checked against egg yolk, the pigment identified if available and the drying oils.

3.3.3. Determination of Binding Media using GC

The chromatographic method chosen for the determination of the organic binding media was the one of ethyl chloroformate derivatives (ECF), which is based on the simultaneous determination of amino acids and fatty acids of proteinaceous, fatty or mixed binding media [31-36]. It is a rapid method, requiring a minute sample quantity, as well as minimum treatment of samples.

The proteinaceous media can be determined with safety based on the seven stable amino acids [37-38]: alanine (A), glycine (G), Valine (V), leucine (L), isoleucine (I), Proline (P), Hydroxyproline (OH). Since each proteinaceous material has a distinct amino acid

composition, the type of the binding medium may be identified from the relative abundance of selected amino acids, as obtained by measuring the relevant peak areas of the gas chromatogram.

Furthermore, based on the ratio of the following fatty acids: azelaic (C_9), palmitic ($C_{16:0}$), oleic ($C_{18:1}$), stearic ($C_{18:0}$), the type of mixed binding media (egg/oil emulsion and type of oil) can be identified.

Materials

Chemicals and Reagents: Ethyl chloroformate (ECF) was purchased from Merck, pyridine, chloroform, were obtained from Fluka.

Reference materials: amino acid standard (Sigma, St. Louis, MO, USA), palmitic acid, stearic acid, oleic acid and azelaic acid (Fluka). The artificially-made samples were prepared in the Laboratory of De Montfort University.

Analytical procedure

The analytical procedure consisted of three main steps: acid hydrolysis, derivatization (ECF derivatives of AA and FA) and chromatographic analysis.

Hydrolysis

The samples were placed in Pyrex tubes with screwed Teflon caps, at which 150 μl of HCl were added. The hydrolysis lasted for 24 h at 110^0C. During hydrolysis proteins were transformed into amino acids and fats into fatty acids. After the hydrolysis they were neutralized with (0,035 g) $CaCO_3$.

Derivatization

50μl of the hydrolyzed sample was treated with 50 μl of ethanol/pyridine (4:1v/v) and 15 μl of ECF were added by briefly

stirring the tube. At the end of the reaction, which lasted about 20 sec, the derivatives were extracted with 50 μl of chloroform. 1μl of the organic phase was injected into the column.

Analysis

A model 8700 gas chromatograph (Perkin Elmer) with a flame ionization detector was employed. Helium was used as the carrier gas. The chromatographic separations were achieved on a 15m x 0.25mm ID column from Restek (RTX-1701), according to the following temperature program: The initial temperature was 70^{o}C for 1 min, and then it was increased at 27^{o}C /min up to 250^{o}C, where it was maintained for 10 min. The injector and detector temperatures were 240^{o}C and 260^{o}C, respectively. The helium head pressure was 17 psig. The split ratio was 20:1. The relative standard deviation (RSD) was less than 5% on 5 subsequent runs for each sample.

3. Results and Discussion

4.1. Physicochemical Research

Two samples V1 and V2 were taken from the panel painting. The sampling area was chosen due to the thickness of the paint layer.

SEM-EDX

The results from samples V1 and V2 are shown in Table 1, Figures 3-4. The results are quite interesting since it seems that the artist used a combination of red lead Pb_3O_4 mixed with cinnabar, HgS. According to artists' manuals this mixture was used a lot by the painters of the time because cinnabar was quite expensive to be used alone and red lead an adequate additive in order to produce the desirable hue. The quantity of calcium detected in the sample, may be a contamination coming from the ground layer, which is calcium carbonate, $CaCO_3$. Finally, the minute quantities of Al and Cl seem to be contaminations from nearby pigments or impurities.

Sample	C	O	Al	S	Cl	K	Ca	Hg	Pb
V1	43.19%	18.44%	0.11%	5.92%	0.56%	-	2.79%	22.63%	6.35%
V2	53.54%	14.15%	0.28%	5.17%	0.60%	0.19%	3.30%	17.52%	5.26%

Table 1. EDX quantitative results of samples V1 & V2

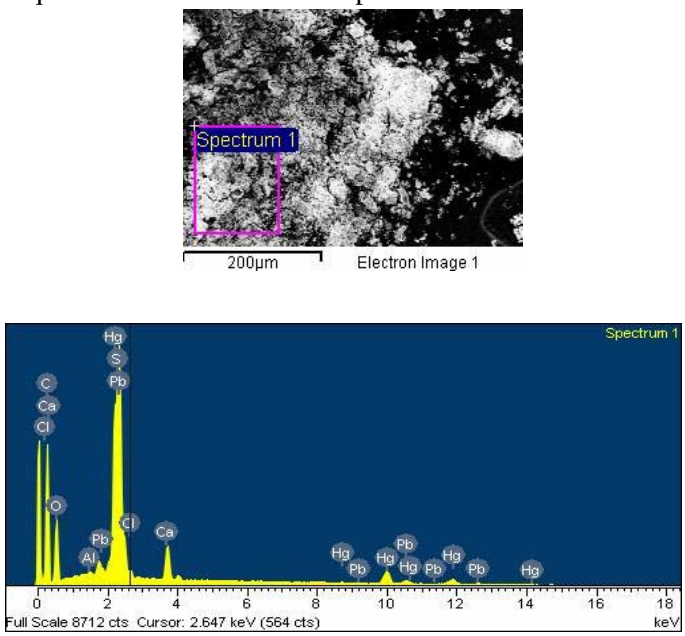

Figure 3: SEM/EDX results of V1

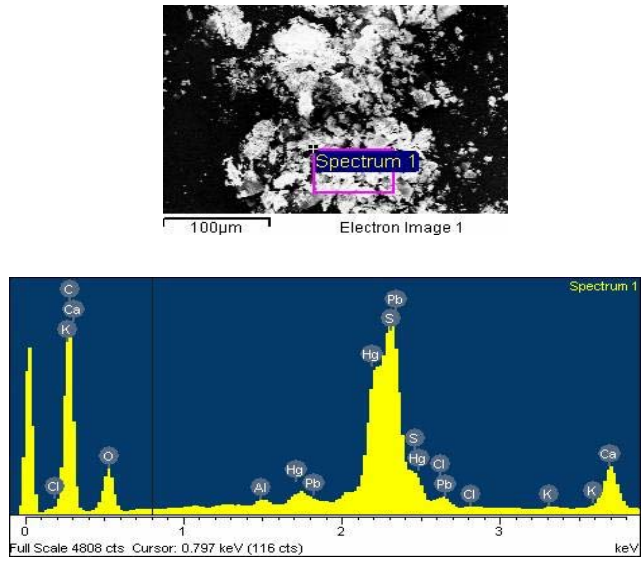

Figure 4: SEM/EDX results of V2

μFTIR

The infrared spectra of the two samples were quite similar. Figures 5-6 show the FTIR spectra. The interpretation (Table 2) of these samples was quite difficult. They seem to contain more pigment than medium and this might be the reason for the absence of the 1740 and 1165cm^{-1} absorption bands, which characterise the triglyceride ester linkages. However, the presence of egg yolk was detected at the 3080 and 3006cm^{-1} bands. Similarly, the presence of red lead was detected at the 1424.1 and 710.3/715.5cm^{-1} bands. Cinnabar does not produce a spectrum at the mid-infrared region therefore it cannot be detected. Finally, no bands leading to the presence of oil were detected.

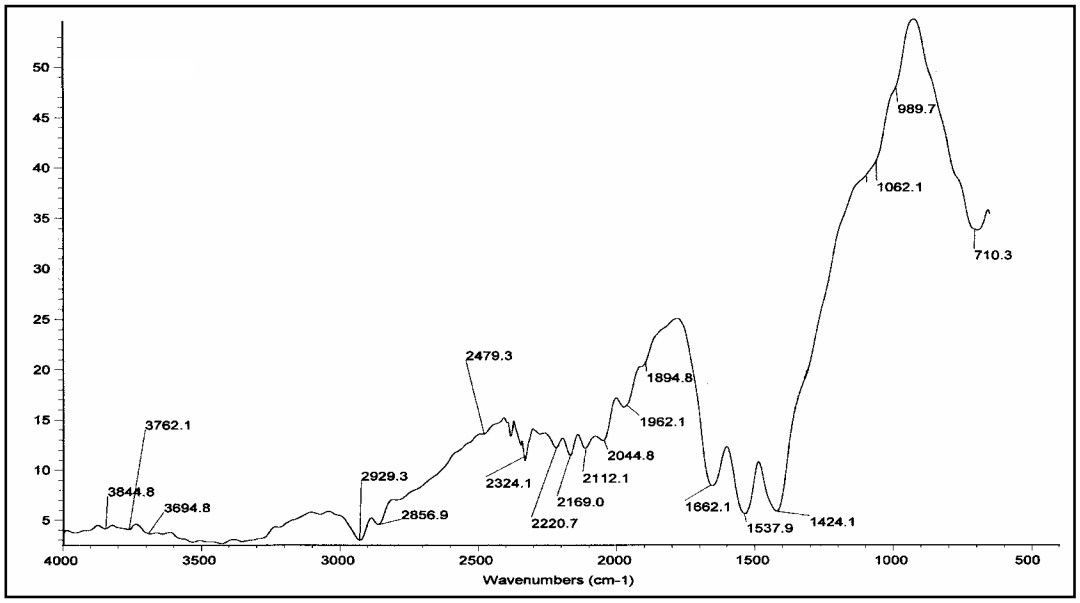

Figure 5: FTIR spectrum of V1

Sample V1	Interpretation	Sample V2
3290 m	N-H stretch	3290 m
3080 vw	Amide II overtone	3080 vw
3006 vw	Lower concentration of unsaturated chains	3006 vw

2929.3 s	CH_2 band	2924.1 s
2856.9 m	CH_2 band	2856.9 m
-	Trygliceride ester linkage	-
1662.1 msh	Amide I [C=O stretch]	1656.9 m
1537.9 m	Amide II	1537.9 m
1424.1 sh	Absorption band due to red lead	1424.1
1300 vwsh	Triglyceride ester linkage	1300 wsh
-	Triglyceride ester linkage	-
1062.1 wsh	Triglyceride ester linkage	1046.6 m
782.8 wsh	Lower concentration of unsaturated chains	782.8 w
710.3 w	Absorption band due to red lead	715.5 m

Table 2: Interpretation chart of FTIR spectra of the samples V1 & V2

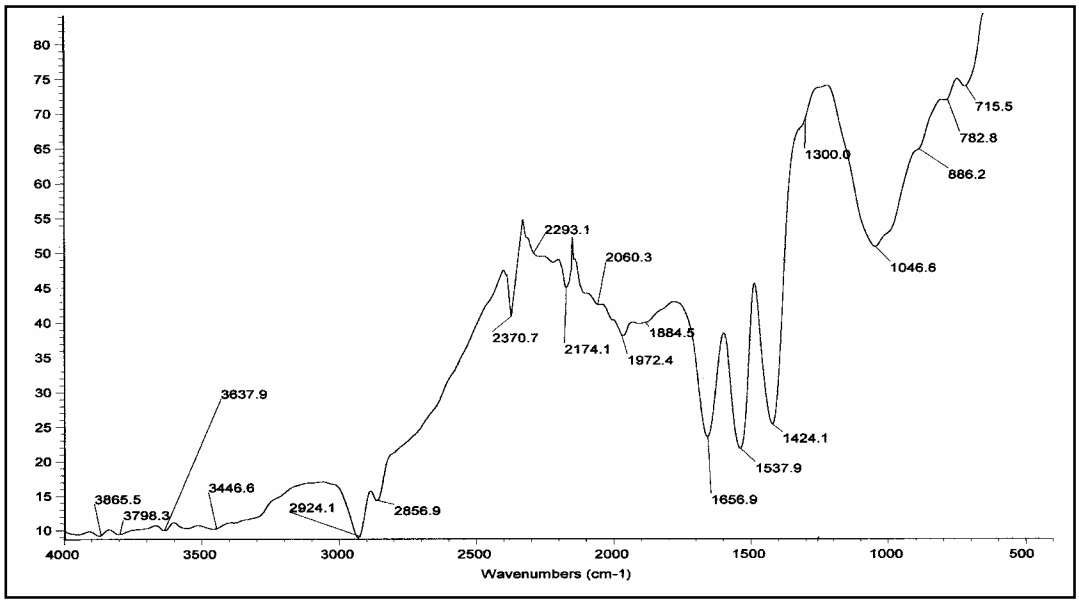

Figure 6: FTIR spectrum of V2

Gas Chromatography

Figure 7 shows the gas chromatogram of the sample V1. The amino acid distribution (Chart 1) and the fatty acid ratios (table 3) suggest that the binding medium of V1 sample is a mixture of animal glue and

egg yolk. The high proportion of Glycine and the presence of Hydroxyproline verify the presence of animal glue. Additionally, the value of the C16/C18 ratio, which is 2.6, suggests the presence of egg yolk.

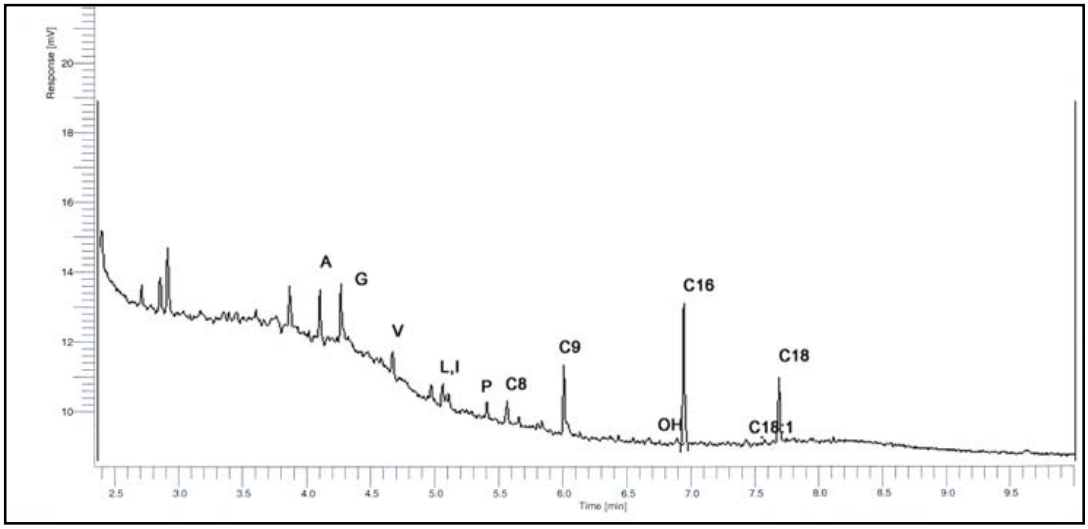

Figure 7: the Gas Chromatogram of sample V1

Sample	C9/C16	C18:1/C18	C16/C18
Egg yolk fresh	0.03 ± 0.02	2.8 ± 0.8	3.2 ± 0.3
Egg yolk aged	0.07 ± 0.02	0.4 ± 0.2	2.5 ± 0.1
V1	0.1	0.0	2.6
V2	0.15	0.0	2.55

Table 3: Comparative table of Fatty Acid relative ratios of egg yolk reference sample and samples V1 & V2

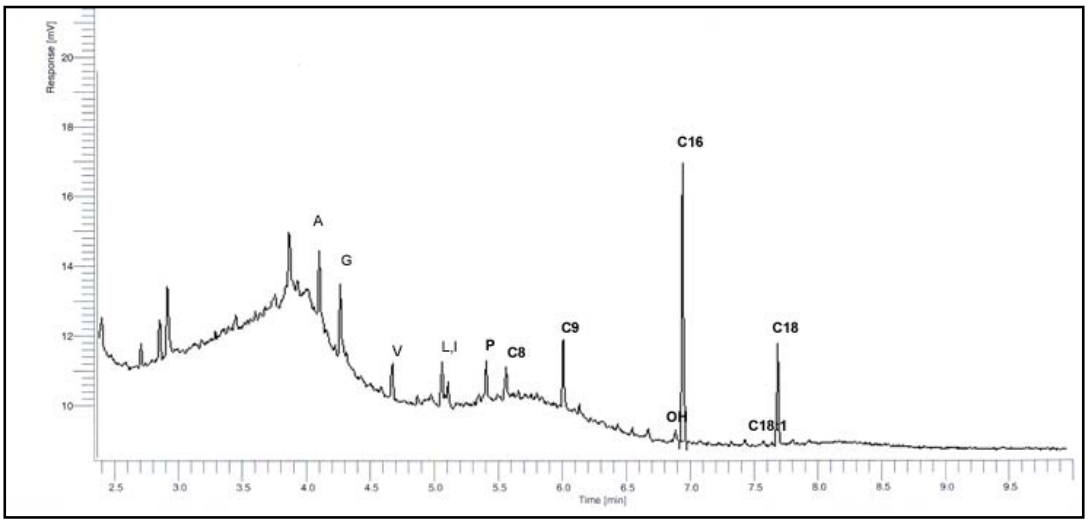

Figure 8 shows the gas chromatogram of the V2 sample. As in V1, the amino acid distribution (Chart 1) and the fatty acid ratios (table 3)

suggest that the binding medium of V2 sample is a mixture of animal glue and egg yolk. The high proportion of Glycine and the presence of Hydroxyproline verify the presence of animal glue. Additionally, the value of the C16/C18 ratio suggests the presence of egg yolk.

Figure 8: the Gas Chromatogram of sample V2

4.2. Conservation Procedure

The condition of the painting was fully recorded and in combination with the information obtained from the analytical research, a conservation procedure was decided. The aim of the treatment was to preserve the artistic and historical integrity of the icon and slow down the degradation process. The conservation laboratory followed all the codes of ethics as they have been defined by the International Conservation Institutes; minimum intervention and reversible materials (Figure 9).

Figure 9: The icon before, during and after conservation treatment

5. Conclusion

The methodology with which this research was approached has proved quite helpful. It can be concluded that:

Energy Dispersive X-ray Analysis was very useful to the identification of the pigments present to the paint samples.

Fourier transform infrared microscopy was useful and successful for the detection of mixtures of pigment and egg tempera.

GC with ECF method of simultaneous determination of AA and FA has proved quite successful for the determination of the exact type of organic binder.

Finally, the physicochemical research of the icon gave important information about the materials and construction method the artist followed. These information were useful for both characterising the style of the painter and for offering a guideline for the conservation treatment of the object.

Acknowledgments

This work was carried out at De Montfort University of United Kingdom and at the National Gallery of Athens of Greece. Thanks are extended to the Reverend Father Antipas Abbot and Patriarchal Exarch of Patmos, Dr M. Doulgeridis (NGA), Panagiotis Asimakopoulos (Perkin Elmer) for GC instruction, Boris Pretzel (V & A) for providing the Irug2000 spectral library, Norma Garrington (DMU) for μFTIR instruction and finally, Eleni Ioakimoglou (Athens TEI) and Agni Terlixi (NGA) for their help with GC methodology.

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