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ANALYTICAL INVESTIGATION OF THE PAINTING TECHNIQUES USED IN ICONS OF THE CRETAN SCHOOL OF ICONOGRAPHY

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ABSTRACT

The painting techniques used in seven icons (15th – 17th cent.) of the Cretan School of iconography were investigated in detail. Microsamples (<<1mg) were extracted from the artworks, which are linked to some prominent representatives of the Cretan School. The cross section of the microsamples were observed by Optical Microscopy (OM) in the Vis and in the UV light to reveal (i) the existing stratigraphies and (ii) any later interventions that were performed on top of the original colouring layers. Micro-Fourier Transform Infra Red (μFTIR) and μRAMAN spectroscopies were employed primarily for the identification of the inorganic pigments and for the speculation of the origins of the organic materials. The identification of the latter (dyestuffs, binding media and varnishes) was achieved by High Performance Liquid Chromatography coupled to a Photodiode Array Detector (HPLC-PDA) and Gas Chromatography with Mass Spectrometry (GC-MS). The results revealed the rich variety of the materials and the sophisticated painting techniques applied by the painters of the Cretan School. Organic dyes, such as kermes, cochineal, madder, soluble redwood and indigoid dyes were used as exclusive colouring matters (or glazes) or in mixtures with inorganic pigments, such as lead white and carbon black. The use of gelatine in the gesso ground was first observed by OM and then confirmed by amino acid quantitative measurements performed by GC-MS. The latter showed that in some icons egg yolk was used as binding medium for the painting layers. Other organic materials which were found in the samples are linseed stand oil, walnut oil, wax, turpentine and synthetic resins.

INTRODUCTION

The identification of the materials, contained in objects of archaeological interest is important for the documentation and conservation of the artworks and may reveal important historical information with respect to the origin of the tested art objects and the technology used for their production. Along this line a multi-method approach has been developed for the characterization of materials used by some great eponymous artists of the Cretan school of iconography. Optical Microscopy (OM), μFTIR, μRaman, HPLC-PDA and GC-MS were employed to investigate in detail the materials contained in microsamples which were extracted from the icons of table 1. An example of the artworks is shown in figure 1.

Table 1. Icons from the Benaki Museum (Athens, Greece)

a/a	Icon	Creator	Date
1	The Virgin of Tenderness (2984)	E. Lambardos	1609
2	The Annunciation (2992)	E. Tzafournaris	late 16th cent.
3	St. Spyridon and scenes from his life (3009)	T. Poulakis	2nd half of 17th cent.
4	Virgin and Child enthroned (3051)	A. Ritzos	2nd half of 15th cent.
5	The seven sleepers of Ephesos (3054)	E. Tzanes	2nd half of 17th cent.
6	Anne and Virgin (31)	A. Akontatos workshop	middle of 15th cent.
7	Virgin and Child (3049)	workshop	2nd half of 15th cent.

Figure 1. Icon 3009 (Benaki museum).

EXPERIMENTAL

The surface of the microsamples and their cross sections were studied and photographed with optical polarizing microscope in white reflected and under UV light employing a polarizing Zeiss Axiotech 100 HD microscope equipped with a complete system of white reflected and ultraviolet source of light, and a Spot 2 1.4 digital cooled camera (res.: 1315 x 1033, 12 bits per colour).

A Renishaw System 1000 micro-Raman spectrometer comprising an Olympus BH-2 imaging microscope, a grating monochromator and a charged-coupled device (CCD) Peltier-cooled detector were employed for Raman spectra acquisition. A HeNe laser (632.8nm) served as the excitation source. A set of two notch filters with a cut-off edge of ~+100 cm^{-1} was employed for the rejection of Rayleigh scattered light. The resolution was kept at ~5cm^{-1}.

FTIR spectra were acquired using a Biorad FTS 175 FTIR spectrophotometer equipped with a UMA 500 microscope. The samples were placed on the surface of a KBr pellet and the spectra were collected at 4 cm^{-1} resolution representing averages of 64 scans.

For liquid chromatography the following solvents were used: HPLC grade acetonitrile (CH_3CN, Merck), trifluoroacetic acid (TFA, Merck) and type I reagent grade water which was produced by a Barnstead EASYpure water purification system. Solvents utilized in the HPLC instrumentation were filtered through a 0.2 μm filter prior to use. Historical samples were treated with pro-analysis grade hydrochloric acid 37% (HCl, Riedel-de Haën), HPLC grade methanol (MeOH, Merck), type I reagent grade water and HPLC grade dimethylformamide (DMF, Riedel-de Haën) according to the known hydrolysis procedure: (i) Samples are treated with a solution mixture of H_2O:MeOH:37%HCl (1:1:2, v/v) at elevated temperature (100^oC). (ii) Then samples are evaporated (50-60^oC) under gentle nitrogen flow. (iii) The dry residues are dissolved in DMF, centrifuged and submitted to HPLC.

Liquid chromatography was carried out using Thermoquest (Manchester, UK) HPLC system consisted of P4000 quaternary HPLC pump, SCM 3000 vacuum degasser, AS3000 auto sampler with column oven, Reodyne 7725i Injector with 20µl sample loop and Diode Array Detector UV 6000LP. Chromatographic separation was carried out on an Alltima HP C18 5µm column with dimensions 250mm x 3.0mm (Alltech Associates, Inc., USA). The column was thermostatted at 33 ^{o}C. The gradient elution program utilized two solvents (A) H_2O-0.1% TFA and (B) CH_3CN-0.1% TFA and the flow rate was 0.5ml/min. Initial of 95% A evolved to 5% within a time period of 35min.

Gas chromatographic analysis was performed with a Hewlett-Packard 5890 II GC (Palo Alto, CA, USA) coupled to a Hewlett-Packard MS Engine 5989A mass spectrometric detector (Waldbronn, Germany). An Ultra 2 (Agilent, USA) column was used od 50 m x 0.20 mm x 0.25 µm film thickness. The carrier gas was helium (purity >99.999%) at an inlet pressure of 100 kPa. Oven programmes: *(a) Analysis of oils, resins and waxes:* 50°C (1 min), ramp of 10°C /min to 320°C (12 min). *(b) Analysis of proteinaceous materials:* 100°C (1 min), ramp of 5°C /min to 300°C. Injector temperature was 300°C (splitless injection), transfer line temperature 280°C, ion source temperature 200°C and quadrupole temperature was 100°C. MS operating conditions were set as follows: Solvent delay: 10 min, electron impact ionisation (70eV), scan rate 1 scan/s over the range m/z 50–550. Electron impact ionization (EI) mass spectra were measured in the total ion monitoring mode and the peak area (TIC) data were used for quantitative investigations.

Standards of eighteen naturally occurring amino acids were purchased from Fluka (Steinheim, Germany). A solution of all amino acids at 1 mmol/l was made in 0.1 N HCl. Five of the most frequently encountered fatty acids (FAs) in oils were considered. They are suberic acid (Su), azelaic acid (Az), palmitic acid (Pa), stearic acid (St), oleic acid (Ol) which were all purchased from Fluka (Steinheim, Germany) with a purity of at least 97%. TMSH was obtained from Macherey–Nagel (Düren, Germany) as a 0.2 mol/L solution in methanol. ECF (purity ≥98%) was obtained from Fluka (Steinheim, Germany).

The sample preparation procedure, prior to GC-MS analysis, includes two steps as follows: Step One: Sample Preparation Procedure for GC-MS Analysis of Oils, Resins and Waxes: Sample preparation is performed directly on the solid sample (less than 0.1 mg) in the PE vials in which they were supplied. 50 µl chloroform is added, and the suspended sample quantitatively transferred to a micro-reaction vial. The sample vials are rinsed twice with 50 µl chloroform, all solvent is transferred to the reaction vial and the solvent evaporated to dryness. 20 µl chloroform are added, followed by 10 µl of TMSH reagent, and then shaken thoroughly; completion of the reaction and dissolution is achieved by ultrasonication for about 1 hour. The sample is allowed to rest for another 3 hours to dissolve as far as possible; centrifugation to sediment the pigments; injection of 2µl of the solution into the GC-MS. Step Two: Sample Preparation Procedure for GC-MS Analysis of Proteinaceous Materials: The reaction mixture from the first step of analysis (for oils, resins and waxes) is evaporated to dryness. 100 µl of 6N HCl are added, and the sample is hydrolysed under argon environment, at 105°C for 24 hours. After hydrolysis, the hydrochloric acid is evaporated under a stream of nitrogen at 70°C. The residue is washed with distilled water which is subsequently evaporated under a stream of argon, repeating this procedure twice. 100 µl of pre-mixed solvent (water: ethanol : pyridine = 60:32:8) are added to the residue, the mixture shaken thoroughly, and 10 µl of ECF reagent added to the mixture and shaken again. After completion of the reaction, 100 µl of chloroform containing 1% ECF are added and shaken thoroughly. Then, 100 µl saturated $NaHCO_3$ solution is added, shaken, and centrifuged to

obtain two clear separated phases. The upper layer is withdrawn and disposed of; 2μl of the organic (lower layer) are injected.

RESULTS AND DISCUSSION

Microscopic and Spectroscopic Results

Examination of samples' surface (figure 2) and of their cross sections (presented later) with optical polarizing microscope (OM) in white reflected and under UV light revealed significant information on the painting technique. The organic pigments were accurately located and details regarding their application (glazes or in mixture with inorganic pigments) were elucidated. The whole stratigraphy was disclosed and it was possible to study the combinations of paint layers, pigment mixtures and their grain sizes, the thickness of paint layers and the presence of old and more recent varnishes. The results obtained by OM are discussed later, in the light of spectroscopic and chromatographic identifications, described next.

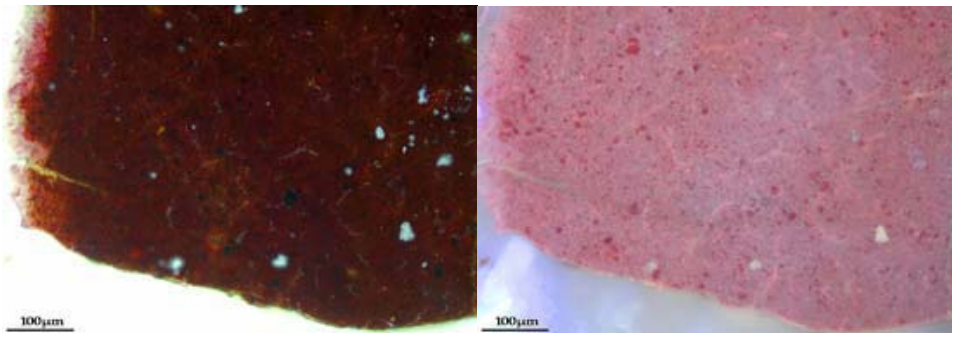


Figure 2. Photomicrographs of sample's surface in reflected and under UV light (underpaint in Virgin's mantle, icon 2984).

Micro-Raman spectroscopy was employed for material identification in cross sections, namely for inorganic minerals and pigments (figure 3), based on characteristic vibrational modes, summarized in table 2. The results of icon samples collected from Raman are described in table 3.

Table 2: Characteristic peaks and relative intensities of pigments analyzed with μRaman spectroscopy [Bell et al., 1997, Burgio et al., 2001] .

Pigment	**Composition**	**Characteristic peaks and relative intensities[1] (cm^{-1})**
Red Ochre	Fe_2O_3	224s, 290vs, 409m
Minium	Pb_3O_4	550s
Azurite	$2CuCO_3.Cu(OH)_2$	402s, 763w, 840m
Lead white	$2PbCO_3.Pb(OH)_2$	1057s
Carbon black	C	1327br, 1590br

([1]vs: very strong, s: strong, m: medium, w: weak, br: broad)

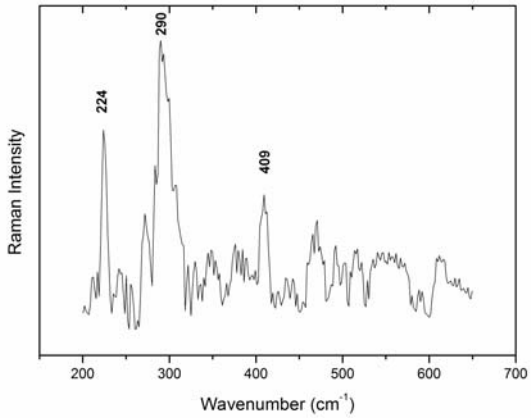


Figure 3. Raman spectrum of red ochre acquired from the underpaint of the cross-section of the sample extracted from icon 2984.

Table 3: Results of micro-Raman analysis

Icon	Sample	Layer	Material
2984	Underpaint in Virgin's mantle	Underpaint	Red Ochre, Carbon Black
2992	Highlight in Virgin's mantle	Underpaint	Red Ochre, Carbon Black
3009	Outline in Saint Spyridon's phelonion	Underpaint	Lead White
3051	Highlight in Saint Nicolas's Phelonion	Highlight	Azurite, Carbon Black
3054	Highlight in Saint Dionysios's cloak	Underpaint Light	Minium Lead White
31	Highlight in Virgin's tunic	Underpaint	Cinnabar
3049	Highlight in Virgin's mantle	Underpaint Highlight	Red Ochre, Carbon Black Lead White

With the application of micro-FTIR spectroscopy it was possible to identify several types of organic materials in each sample by their major functional groups. Characteristic absorption peaks of oil and protein were detected in all spectra. In most cases resin peaks were also observed. Oil identification was based on the characteristic carbonyl stretching mode νC=O at 1730 cm^{-1}, the peaks at 2930 and 726 cm^{-1} due to νC-H stretching γC-H bending, respectively. The amide I stretching vibration νC=O at 1650 cm^{-1} and the amide II combination band δN-H and νC-N at 1547 cm^{-1} denoted the presence of protein. Resin peaks were recorded at 1720 cm^{-1} (the amide I vibration) 1250 and 1040 cm^{-1} (νC-O modes) [Derrick *et al.*, 1999]. The results are summarized in table 4.

Table 4: Results of micro-FTIR analysis

Icon	Material	Icon	Material
2984	Oil, Protein, Resin	31	Oil, Protein, Resin
2992	Oil, Protein, Resin	3054	Oil, Protein, Resin
3051	Oil, Protein	3009	Oil, Protein, Resin

HPLC Results

HPLC was used to identify the organic colorants contained in the samples which were extracted from the icons of table 1. The results are summarized in table 5. Figure 4 shows the chromatogram which corresponds to the sample of icon 3051. We note that Bra´ and compound named as "type C" are components of soluble redwoods [Nowik, 2001].

The identification of carminic acid (major component of cochineal) in samples extracted from icons 2984, 2992, 3009 and 3054 indicates the presence of cochineal. Minor components of cochineal such as kermesic acid, flavokermesic acid, dcIV and dcVII were also detected. The use of a madder source is reported for icons 2992 and 3051. In the latter alizarin and purpurin were detected as shown in figure 4. In the sample extracted from icon 2992 only alizarin was found. Small quantities of indigotin were detected in samples extracted from icons 3009 and 3051. Kermesic and flavokermesic acids (but no carminic acid) were identified in the sample of icon 3051, leading thus to the conclusion that kermes was used by the iconographer of this artwork. Finally, no organic dye was detected in the sample extracted from icon 31.

Table 5. Organic colouring compounds identified by HPLC

Icon	Colouring components
2984	Carminic acid, dcIV, dcVII, Kermesic acid, Flavokermesic acid
2992	Carminic acid, dcIV, dcVII, Kermesic acid, Flavokermesic acid, Alizarin
3009	Carminic acid, dcIV, dcVII, Kermesic acid, Flavokermesic acid, Indigotin
3051	Bra´, type C compound, Kermesic acid, Flavokermesic acid, Alizarin, Purpurin, Indigotin
3054	Carminic acid, dcIV, dcVII, Kermesic acid, Flavokermesic acid
31	-
3049	Kermesic acid, Flavokermesic acid

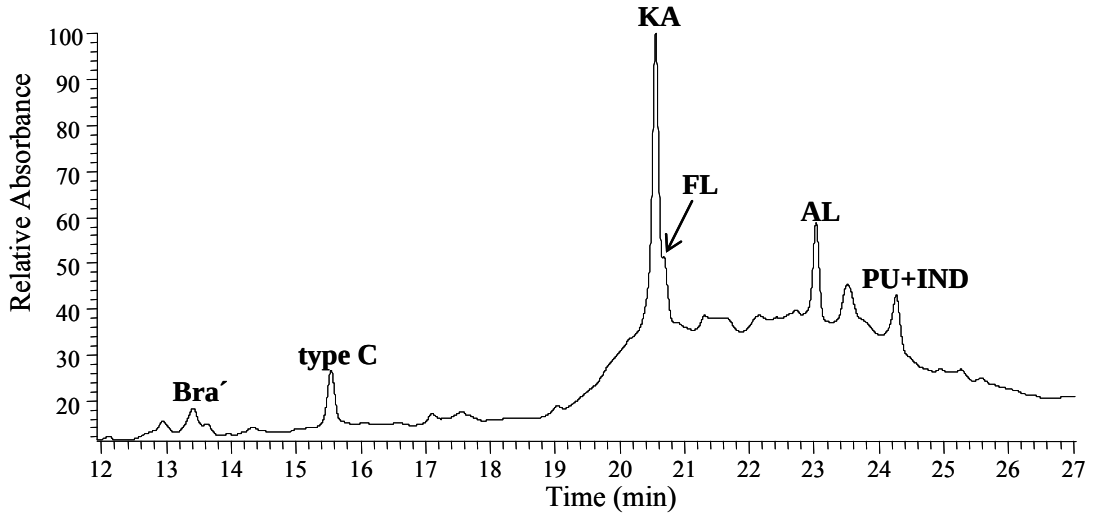
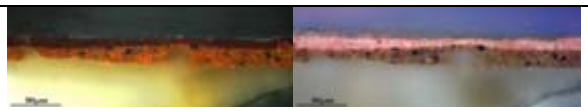
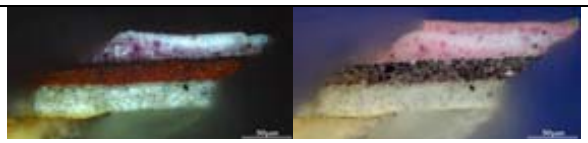
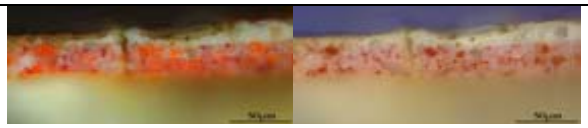
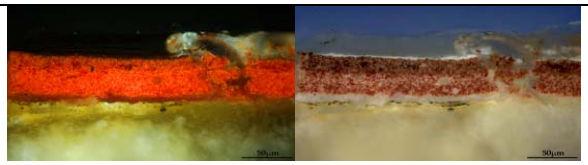
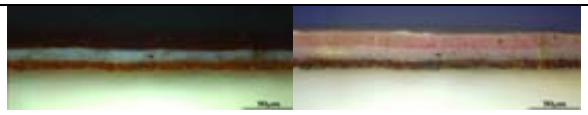


Figure 4. HPLC chromatogram of sample extracted from icon 3051 collected at 254nm. Peaks which correspond to brazilein derivative (Bra´), type C compound (type C), kermesic acid (KA), flavokermesic acid (FL), alizarin (AL), purpurin (PU) and indigotin (IND) are shown. PU and IND are eluted in mixture (not separated).

Stratigraphies

The results obtained by OM, FTIR and Raman spectroscopies and HPLC are summarized in table 6. HPLC was used for the identification of natural organic dyes. Other organic materials were identified by GC-MS, discussed in the following paragraph.

Table 6. Stratigraphies of the investigated icons

Icon	Sample	Cross-section	Stratigraphy
2984	Underpaint in Virgin's mantle		Underpaint: red ochre, carbon black Glaze: cochineal Restoration varnish
2992	Highlight in Virgin's mantle		Gold halo: yellow bole - gold leaf Underpaint (building): lead white, carbon black Underpaint (mantle): red ochre Outline: carbon black Light: cochineal and madder, lead white Highlight: lead white Glaze: cochineal and madder
3009	Outline in Saint Spyridon's phelonion		Underpaint: cochineal, lead white Shadow: cochineal Outline: cochineal, indigo Glaze: cochineal Original varnish
3051	Highlight in Saint Nicolas's phelonion		Underpaint: red ochre Light: lead white, red ochre Highlight: lead white Glaze: mixture of redwood, kermes and madder Original varnish Restoration varnish
3054	Highlight in Saint Dionysios's cloak		Underpaint: cochineal, minium, lead white Light: lead white Original varnish
31	Outline in Saint Anna's mantle		Gold background: yellow ochre - gold leaf Varnish Underpaint: minium Outline: cinnabar Original varnish Restoration varnish
3049	Highlight in Virgin's mantle		Underpaint: red ochre, carbon black Light: lead white, red ochre Highlight: lead white Glaze: kermes Original varnish Restoration varnish

GC-MS Results

After derivatization with TMSH samples were analysed with GC-MS. Carboxylic acids, including azelaic acid, palmitic acid and stearic acid have been found in all seven samples, and the peak area ratios of azelaic acid to palmitic acid (A/P) and palmitic acid to stearic acid (P/S) have been calculated (table 7), indicating the presence of drying oil in the samples. Since the value of the A/P ratio for linseed oil is 0.2 and 0.3, this indicates that the linseed oil probably has been heat bodied [Wei, 2007].

In addition to the fatty acid esters, antioxidant compounds for synthetic resin have been detected in all the samples, including 2,4-*bis*-(1,1-dimethylethyl)-phenol and methyl-3-(3, 5 di-*tert.*butyl-4-hydroxy-phenyl)-propionate. This means that synthetic resin may have been introduced in the painting during later restoration. This is confirmed by the cross-section photomicrographs (table 6) which reveal layers of later interventions.

In some samples adipic acid and oleic acid have been detected. Adipic acid is one of the oxidization products of oils while oleic acid is originally present in drying oils. Finally, in some samples 7-oxo-DHA (dehydroabietic acid) and 15-OH-7-oxo-DHA and a series of alkanes have been detected, indicating the presence of turpentine and traces of wax.

Table 7. P/S and A/P ratios after GC-MS analysis

Icon	P/S	A/P	Icon	P/S	A/P
2984	1.6	0.2	3054	1.9	0.2
2992	2.2	0.2	31	1.7	0.1
3009	1.8	0.2	3049	1.4	0.3
3051	2.1	0.4			

The sample residues from the first step of analysis were derivatized with ECF and subjected to GC-MS analysis. Amino acids have been identified in the all seven samples, indicating the presence of proteinaceous materials. According to the profile of the amino acids, animal glue can be concluded to be present in all samples apart from sample extracted from icon 3049. The latter was the only sample that did not contain any gesso ground in which animal glue was very often used. The profile of amino acids in sample extracted from icon 3049 is similar as in egg yolk, indicating the use of this material as a binding medium.

The materials identified by GC-MS are summarized in table 8.

Table 8. Organic materials identified by GC-MS

Icon	Materials Found
2984	Linseed stand oil, gelatine, wax, turpentine, synthetic resin
2992	Walnut oil , gelatine, synthetic resin
3009	Linseed stand oil, gelatine, synthetic resin
3051	Walnut oil, gelatine, synthetic resin
3054	Walnut oil and linseed oil, gelatine, synthetic resin
31	Walnut oil and linseed oil, turpentine resin, trace of egg yolk, trace of wax, synthetic resin
3049	Linseed stand oil, egg yolk, synthetic resin

CONCLUSION

A multi-method approach has been developed for the characterization of materials used by some great eponymous artists of the Cretan school of iconography. Optical Microscopy, μFTIR, μRAMAN, HPLC-PDA and GC-MS were employed to investigate in detail the materials contained in microsamples which were extracted from seven icons.

Red Ochre, minium, azurite, lead white, carbon black were found to have been used by the artists of the Cretan School of iconography. The following organic dyed were identified by HPLC-PDA: kermes, cochineal, madder, soluble redwood and an indigoid dye source. Other organic materials identified in the samples by GC-MS are linseed stand oil, egg yolk, walnut oil, wax, turpentine and synthetic resins.

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