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Project on the Rock Paintings in Cappadocia. Analitycal Investigations of the Church of he Forty Martyrs in Şahinefendi and Other Sites (Report 2008)

Claudia PELOSI - Ulderico SANTAMARIA - Giorgia AGRESTI
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Claudia PELOSI*
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Introduction

This report will relate about the main results of the analyses carried out on the rock paintings of several Cappadocia churches. The analyses have been carried out within the survey *"Rock paintings in Cappadocia. For a project of knowledge, conservation and valorization of the church of the Forty Martyrs at Şahinefendi and its territory"* directed by Prof. Maria Andaloro of

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Tuscia University (Italy)[1]. Such analyses have been carried out according to a methodological path tested during the several years of surveys in Turkey, particularly on the island of Küçük Tavşan and on many other sites in the territory of Mandalya Gulf and also on the occasion of other research projects[2]. This research mission is part of a bigger project called *"For a data bank of wall paintings and mosaics of Asia Minor (4th-15th centuries: images, materials, techniques of execution (1996-2010)"* directed by Prof. Maria Andaloro.

The aim of this work concerns the understanding of the constitutive materials, the execution techniques and the conservation conditions of the rock paintings. For this reason several *in situ* and laboratory analyses have been undertaken.

In the first part of this report the main results of the analyses carried out during the 2008 campaign on the Forty Martyrs Church at Şahinefendi and of a group of churches in the region of Nevşehir will be described. In the second one an overall view on the three years analyses of the materials collected during the surveys will be shortly presented.

The attention will be focused on the pigments of the rock paintings with some reference to the stratigraphic analyses and to the binders of the pigments.

Materials and Methods

The *in situ* investigations have been carried out by means of: a portable video microscope Keyence directly connected to a portable computer through a graphic card and a reflectance spectrocolorimeter X-Rite CA22 model. The spectrocolorimetric analyses were performed according to the CIE 1976

1 M. Andaloro, "Rock Paintings of Cappadocia: Images, Materials, and State of Preservation", in *XXIX International Symposium of Excavations, Survey and Archaeometry*, (Kocaeli, 28 May - 1 June 2007), Ankara 2008, pp. 163-178. M. Andaloro, "Project for the rock paintings in Cappadocia. The church of the Forty Martyrs at Şahinefendi", in *XXX International Symposium of Excavations, Survey and Archaeometry*, (Ankara, 26-30 May 2008), Ankara 2009, 26, pp.187-200.

2 M. Andaloro, "Küçük Tavşan Adası: Final Report 1996-2005", in *XXVIII International Symposium of Excavations, Survey and Archaeometry*, (Çanakkale, 29 May - 2 June 2006), Ankara 2007, 24, pp. 1-14.

method, with a 10nm step of measurement using the standard illumination C/2°. The results are reported as reflectance spectra and L*a*b* color space.

Moreover during the 2008 survey forty six micro samples of plasters, pigments and other materials were collected. The micro samples were examined in the Laboratory of Diagnostics for Conservation and Restoration "Michele Cordaro" of University of Tuscia by means of: an Olympus SZ stereo microscope, a polarizing microscope Zeiss Axioskop equipped with a digital AxioCAM; a Nicolet Avatar 360 DRIFT FT-IR spectrophotometer in association with a Centaurμs FT-IR microscope has been also employed to the purpose.

The micro-Raman analyses were performed in the Raman laboratory, using a Labram Model, Dilor JobinYvon spectrometer equipped with a CCD detector, the exiting wavelength was the 632.8 nm red line of a He-Ne laser. The SEM-EDS (Scanning Electron Microscope - Energy Dispersive Spectroscopy) analysis was carried out in a private laboratory (S.I.R.Am. S.r.l.) by means of a LEO 420 scanning electron microscope, equipped with an ISIS LINK microanalysis system.

Results and Discussion

During the 2008 campaign six churches, indicated by a mark, have been taken under examination:

- Forty Martyrs Church at Şahinefendi (S), 25 samples;
- Ali Reis Kilise at Ortahisar (ARO), 4 samples;
- Cambazlı Kilise at Ortahisar (CKO), 4 samples;
- Hayvali Church (HC), 7 samples;
- Mustafapaşa, S. Basilio (SB), 5 samples;
- S. Apostles Church (SA), 1 sample.

Each measurement and sampling point was marked with a number that indicates the progressive sample and the year of the survey (Fig.1).

The video microscope acquisitions are useful to obtain a high magnification of the painted surface so that mixtures of pigments, alterations, surface abrasions and other particulars can be put in evidence in a totally non invasive modality[3]. Sixty four acquisitions were taken at four magnifications. Figure 2 shows the presence of a diffuse blackening of the red color of the apostle garment in the south apse of the Forty Martyrs Church in Şahinefendi. The subsequent figure (Fig. 3) shows the green color of the apostle face in the south apse of the same church: black and white particles are visible, these last ones probably are due to the mortars layer under the painted surface. Some red particles are visible on the right side of the acquisition, particularly evident at higher magnifications, probably used for the flesh of the face. Figure 4 shows the trunk of the tree in the south apse of the Forty Martyrs Church that appears with a brown color obtained by means of a superimposition of red and black pigments. At last Figure 5 shows a particular of the plaster of the south nave of the Forty Martyrs church, unit βII2: the image at magnification 50x put in evidence the presence of straw fibres added to the mortar.

The color measurements are very important to state the chromatic characteristics of a painted surface (hue, lightness, saturation) and to make hypothesis on the nature of the pigments by comparing the obtained results with literature data[4]. Fifty three color measurements were taken. Figure 6 shows the reflectance spectrum of a yellow surface corresponding to the halo of Saint Damien in the south nave of the Forty Martyrs Church. The presence of an inflection point at about 470 nm indicates that the painting surface contains yellow ochre. The comparison of the colorimetric parameters (L*=43.0, a*=8.83, b*=26.1) with the literature references indicates a greater

3 C. Pelosi, "L'indagine scientifica nei beni culturali: l'esperienza del Laboratorio di Diagnostica per la Conservazione e il Restauro dell'Università della Tuscia" in, *Atti del V Colloquio Internazionale su "Formazione, occupazione e beni culturali e ambientali"*, Salerno 11-14 Dicembre 2000, Roma, 2001, pp. 144-149.

4 R. L. Feller, Editor, *Artists' Pigments. A Handbook of Their History and Characteristics*, Volume 1, National Gallery of Art, Washington, 1986. A. Roy, Editor, *Artists' Pigments. A Handbook of Their History and Characteristics*, Volume 2, National Gallery of Art, Washington, 1993. E. West Fitzhugh, Editor, *Artists' Pigments. A Handbook of Their History and Characteristics*, Volume 3, National Gallery of Art, Washington, 1997. B. H. Berrie, Editor, *Artists' Pigments. A Handbook of Their History and Characteristics*, Volume 4, National Gallery of Art, Washington, 2007.

similarity with the raw umber from Cyprus (L*=36,7; a*=8,9; b*=22,9)[5] but it's very probable that the presence of blackened areas could influence the color making the yellow ochre much more dark than its natural hue.

The reflectance spectrum obtained from the green garment of the apostle in the south apse of the Forty Martyrs church (Fig. 7) shows the probable presence of a green earth; the maximum of the curve is 570 nm indicating a yellowish green (burnt green earth)[6].

The colorimetric analysis puts in evidence also some deterioration forms of the pigments like in the north nave apse. The red color of the wing of the right angel in the right side seems to show some blackening areas. In fact the reflectance spectrum (Fig. 8) and the L*a*b* (L*=8.35, a=7.49, b*=11.2) data have not a clear correspondence with the literature references. The SEM-EDS analyses in this point revealed the presence of iron, lead and mercury[7]. So it is probable that lead and mercury based pigment could be undertaken some alterations.

The polarizing microscope observation together with the FTIR and Raman analyses allowed the detection of the following pigments: hematite, goethite, green earth, vegetable black, ultramarine mixed with other pigments (lead yellow and red, and mercury based compounds and yellow organic lakes, probably saffron)[8].

The green areas are realized with green earths, probably a pure celadonite. In most of the examined samples the pigments seem to be applied by *a secco* or lime technique. The pigments particles, in fact, are not linked to the micritic

5 B. H. Berrie, Editor, *Artists' Pigments. A Handbook of Their History and Characteristics*, Volume 4, National Gallery of Art, Washington, 2007, p. 55.

6 R. L. Feller, Editor, *Artists' Pigments. A Handbook of Their History and Characteristics*, Volume 1, National Gallery of Art, Washington, 1986, pp. 144-146.

7 U. Santamaria, G. Agresti, C. Pelosi, A. Pernella, "Rock Painting's Materials in Cappadocia: Şahinefendi Forty Martyrs Church", in *The XXX International Symposium of Excavations, Surveys and Archaeometry.* (Ankara, 26-30 May 2008) Ankara 2009, 24, pp. 307-316.

8 N. Eastaugh, V. Walsh, R. Siddall, T. Chaplin, *Pigment Compendium - Optical Microscopy of Historical Pigments*, Elsevier Butterworth-Heinemann, Amsterdam, 2006. N. Eastaugh, V. Walsh, R. Siddall, T. Chaplin, *Pigment Compendium – CD ROM*, Elsevier Butterworth-Heinemann, Amsterdam, 2006.

calcite as it was possible to observe in almost all the Canada Balsam mounted slides. An organic yellow dye has been found in sample 33 from Şahinefendi Forty Martyrs Church (Fig. 9). It is characterized by very fine particles adsorbed over a transparent material visible in the figure. The Raman spectra of this sample, measured in the region from 100 to 3000 cm^{-1} revealed the presence of: hematite, goethite, lead compounds (probably lead-tin yellow type I and/or litharge), gypsum and an organic yellow dye (peak at 1567 cm^{-1} with a shoulder at 1604 cm^{-1})[9].

In all the examined samples bi-hydrate sulphate (gypsum) is present. This compound was revealed by means of polarizing microscope observation, FTIR analysis and micro Raman spectroscopy (it shows a typical peak at 1010 cm^{-1} in the Raman spectrum). It is particularly abundant in the micro samples taken from the rock painting of S. Basilio church in Mustafapaşa (Fig. 10). The main bands of gypsum are put in evidence in the infrared spectrum[10].

In many of the examined samples organic materials have been found. These materials are more abundant in the church of Hayvali, Ali Reis Kilise, Cambazlı Kilise and Şahinefendi (Forty Martyrs Church). These organic materials are probably proteinaceous binders and in some cases restoration compounds. In Figure 11 the FTIR spectrum of a micro sample from the Hayvali Church is showed. The single C-H and double C=O organic bond stretching are put in evidence. The iron-oxygen bond stretching is also showed and it is referred to the presence of iron oxides (hematite and goethite). The cross section of the sample HC5 from Hayvali Church shows that the green color is applied over a white layer made of gypsum characterized by a punctiform orange fluorescence in UV observation. The mortar is made of calcite and rare brown, red and transparent aggregates with some yellow UV fluorescence (Fig. 12).

9 L. Burgio, R.J.H. Clark, "Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation", in *Spectrochimica Acta Part A*, 57, 1471-1489.

10 M.R. Derrick, S. Stulik, J.M. Landry, *Infrared Spectroscopy in Conservation Science*, The Getty Conservation Institute, Los Angeles, 1999. I. Adrover Gracia, *Applicazioni della spettrofotometria IR allo studio dei beni culturali*, Collana i Talenti, Il Prato, Padova, 2001. P. Griffiths, J.A. Haseth, *Fourier Transform Infrared Spectrometry*, Wiley, Hoboken, 2007.

The natural ultramarine was found only in the Saint Apostles Church (Fig. 13). This pigment was identified by means of polarizing microscope observation, infrared and Raman spectroscopy. The sulphur S^{6+} in the lattice of ultramarine produces a unique IR absorption band at 2340 cm^{-1}[11]. The FTIR analysis put in evidence also the presence of gypsum, calcium carbonate and organic materials, probably proteins.

Most of the examined cross sections of the micro fragments from the plasters show that the mortars are constituted by calcite with few or no aggregates (only in the mortars of the Hayvali church some aggregates are present) and gypsum. This last compound is particularly abundant and evident in the samples from Cambazlı Kilise, Ali Reis Kilise, Saint Basilio. In the Saints Apostles Church gypsum is used as preparatory layer under the ultramarine blue. The mortar of the Şahinefendi Forty Martyrs Church samples contains also vegetable fibres visible in the cross sections.

Overall Results (2006-2008)

All the examined churches within the surveys in Cappadocia, carried out from 2006 to 2008, are reported in Figure 14 together with the analysis results. Totally 19 churches have been studied: Figure 14 shows the examined churches, the number of samples taken from each of them (between brackets), the analytical results for all the examined churches in the three years of the survey. One hundred seventy eight micro samples of pigments, mortars and other materials were taken off. As regards the pigments, hematite, goethite, green earth, vegetable black, ultramarine are used, mixed with other pigments (lead and mercury based compounds) and organic dyes. The most important result is that in many cases the lime plaster receives the pigments probably through the use of an organic binding medium.

The analyses also showed the presence of gypsum in almost all examined samples, often with high amounts. The micro-FTIR analysis, carried out on small areas of the cross sections, showed the presence of gypsum in all the

11 M.R. Derrick, S. Stulik, J.M. Landry, *Infrared Spectroscopy in Conservation Science*, The Getty Conservation Institute, Los Angeles, 1999, pp. 134-138.

mortars with a greater concentration in the area under the painting layer. The gypsum seems to be used in the composition of the mortars together with lime and proteinaceous materials. In some of the examined samples gypsum is the main component of the *intonaco* layer probably used as a surface to paint with organic binding media over a plaster that has undergone a partially or completely carbonation process.

The data for each sample have been collected in a suitable card that reports all the information about the sampling, the carried out analyses, and the obtained results. These cards are very useful as a database of materials and techniques of Cappadocia. The first page of the card reports the data referred to the sampling and the photo of the micro sample (Fig. 15). The subsequent pages show the pigment particles and the cross section examination by means of the polarizing microscope and the obtained results. Then, the spectroscopic analyses are reported: FTIR and micro-FTIR spectra with the main bands; SEM-EDS spectra, when measured, with the concentrations of the elements.

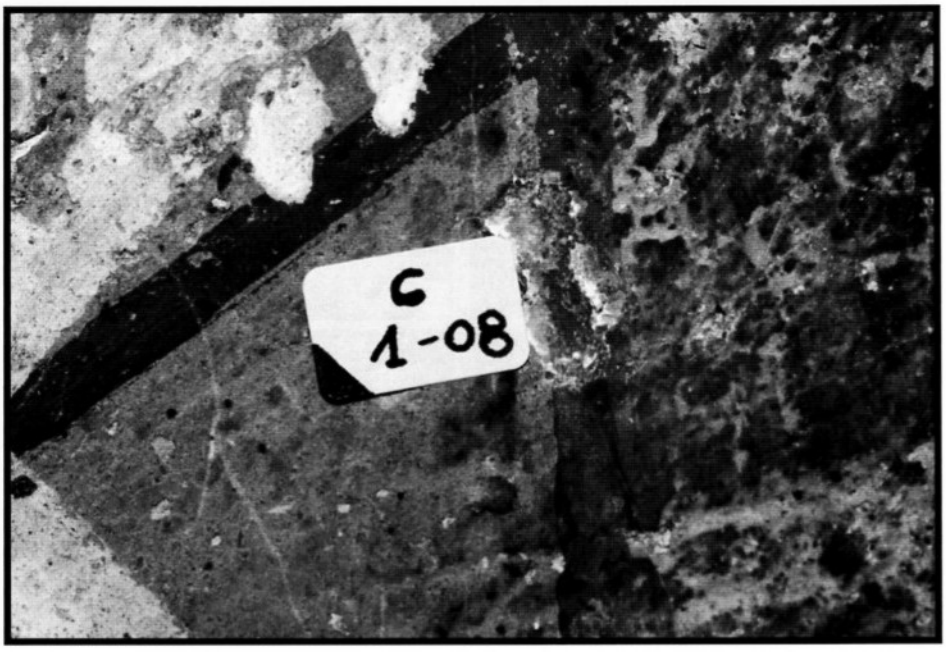

Fig. 1: Şahinefendi, Forty Martyrs Church, point of colorimetric analysis and video microscope acquisition on the garment of the apostle in the south apse, right side.

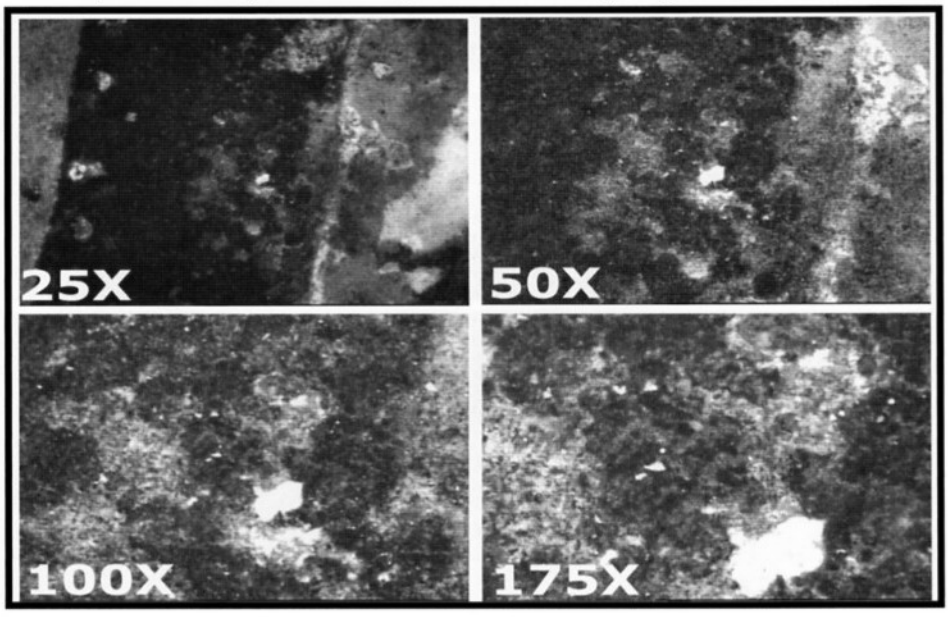

Fig. 2: Şahinefendi, Forty Martyrs Church, south apse, left side. Blackened red color of the apostle garment at four different magnifications.

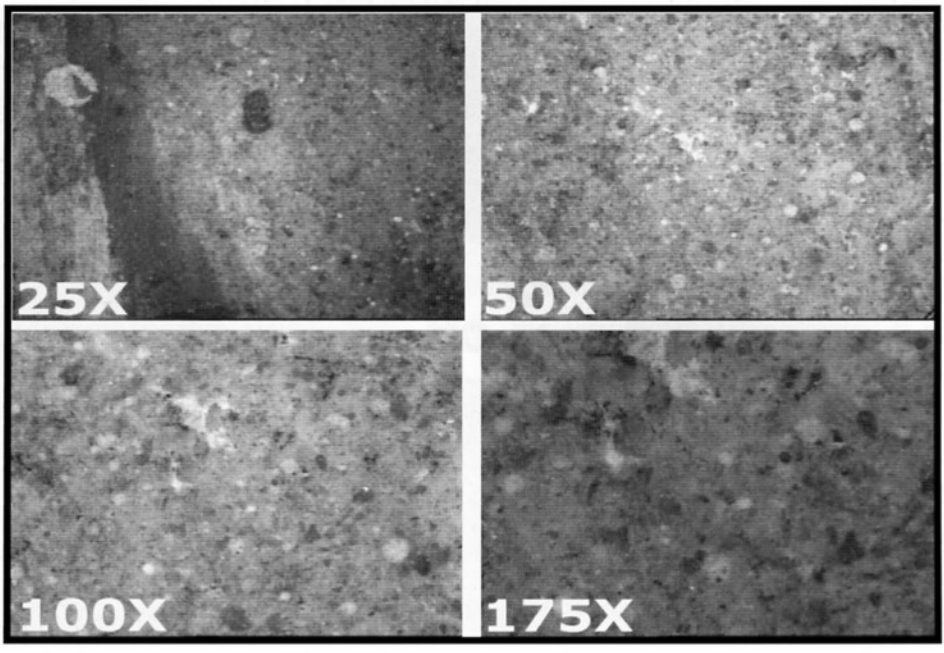

Fig. 3: Şahinefendi, Forty Martyrs Church, South apse. Green color of the apostle face at four different magnifications.

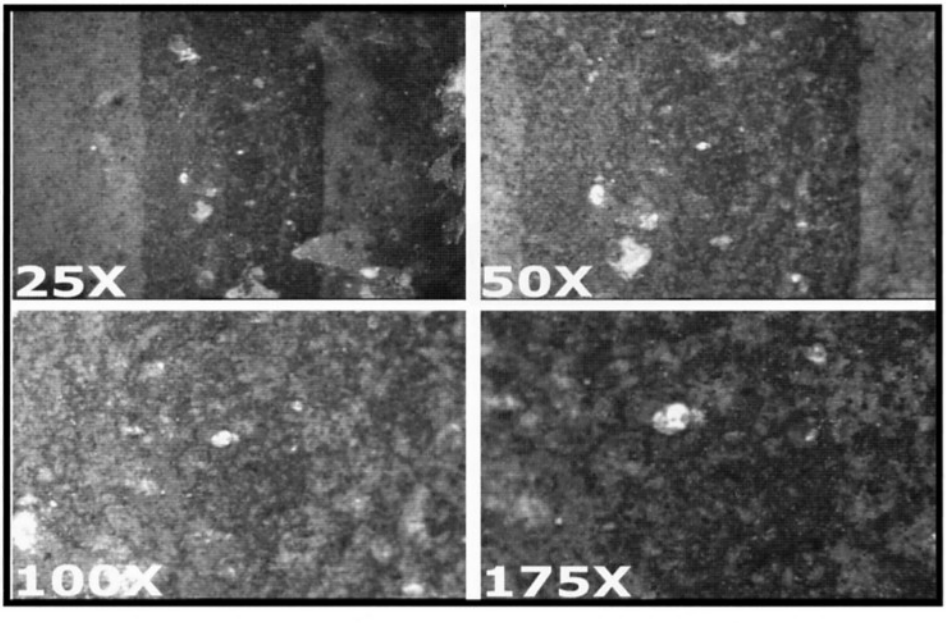

Fig. 4: Şahinefendi, Forty Martyrs Church, south apse, left side. Brown color of the trunk of the tree at four different magnifications.

Fig. 5: Şahinefendi, Forty Martyrs Church, south nave, unit βII2. White plaster with straw, magnification 50x

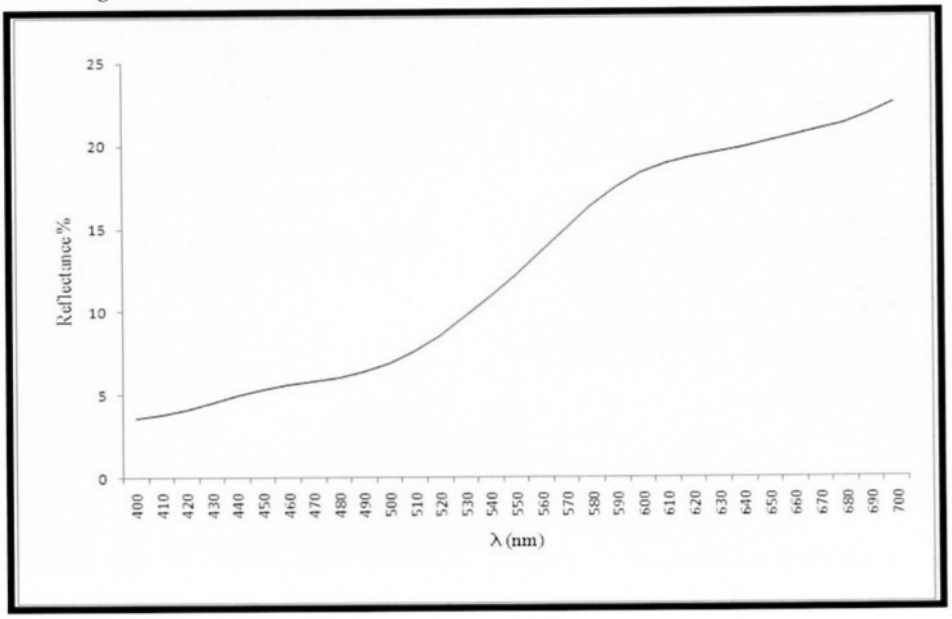

Fig. 6: Reflectance spectrum of the yellow color of the S. Damien halo, Şahinefendi, Forty Martyrs Church, south nave, unit βII2.

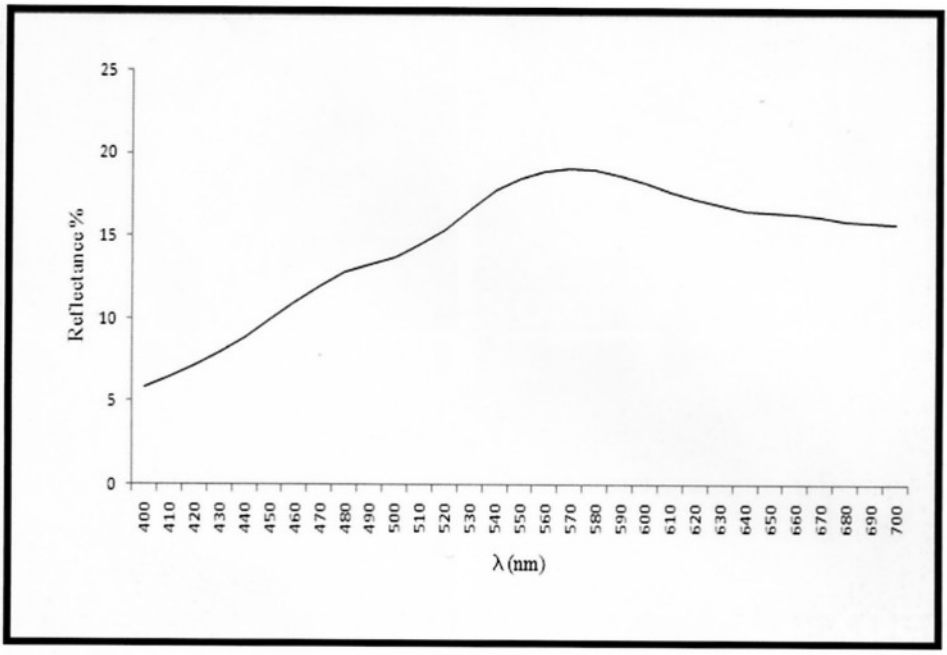

Fig. 7: Reflectance spectrum of the green color of the apostle garment, Şahinefendi, Forty Martyrs Church, south apse.

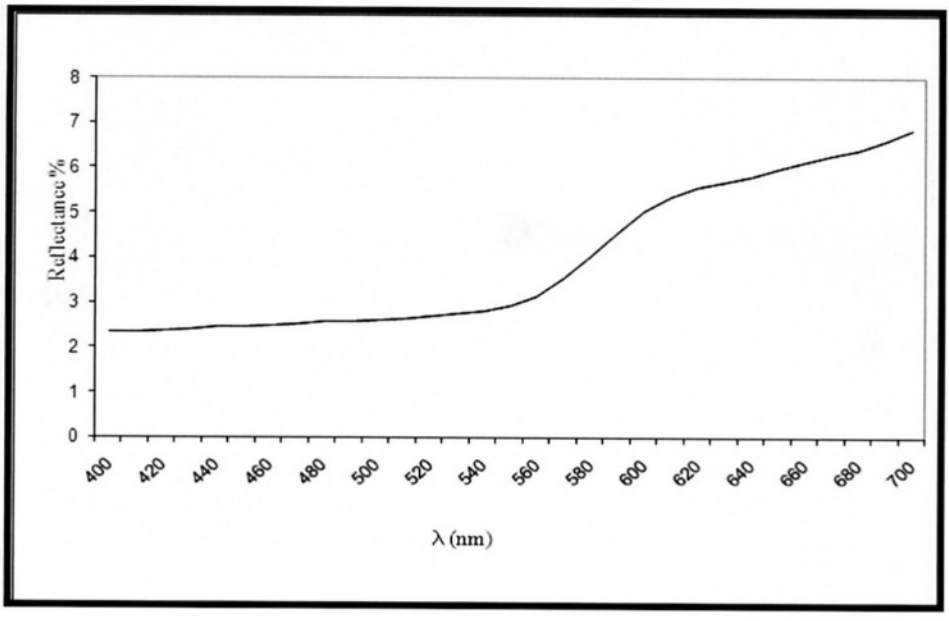

Fig. 8: Reflectance spectrum of the red color of the wing of the right angel, Şahinefendi, Forty Martyrs Church, north nave, apse, right side, unit AI1. The red color in partially blackened.

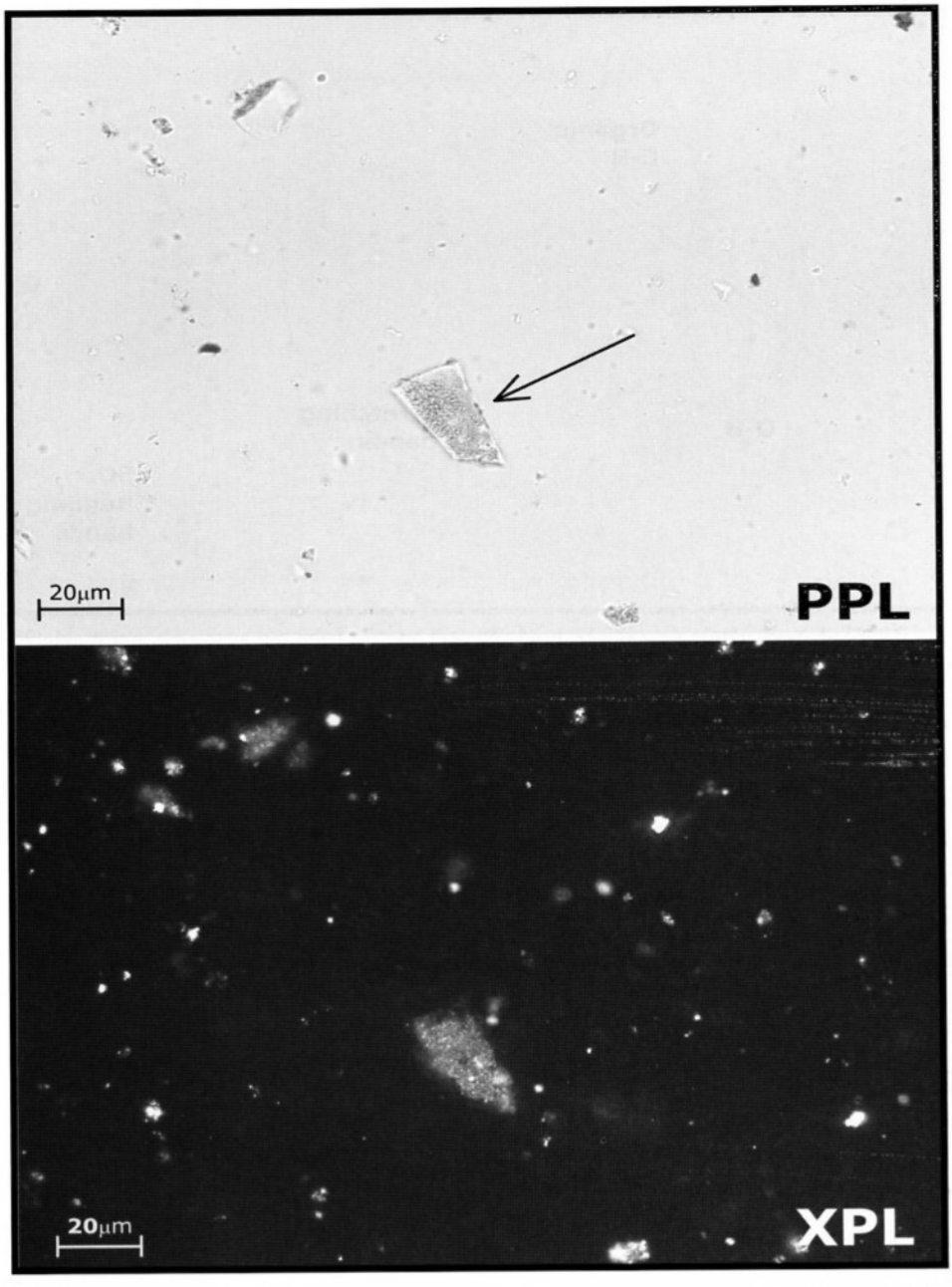

Fig. 9: Pigments from the orange band of the left Angel, Şahinefendi, Forty Martyrs Church, south nave. Polarizing microscope observation, magnification 40x. Gypsum, vegetable black, lead yellow and red based pigments, a probable organic dye (see the arrow in the PPL image) are visible.

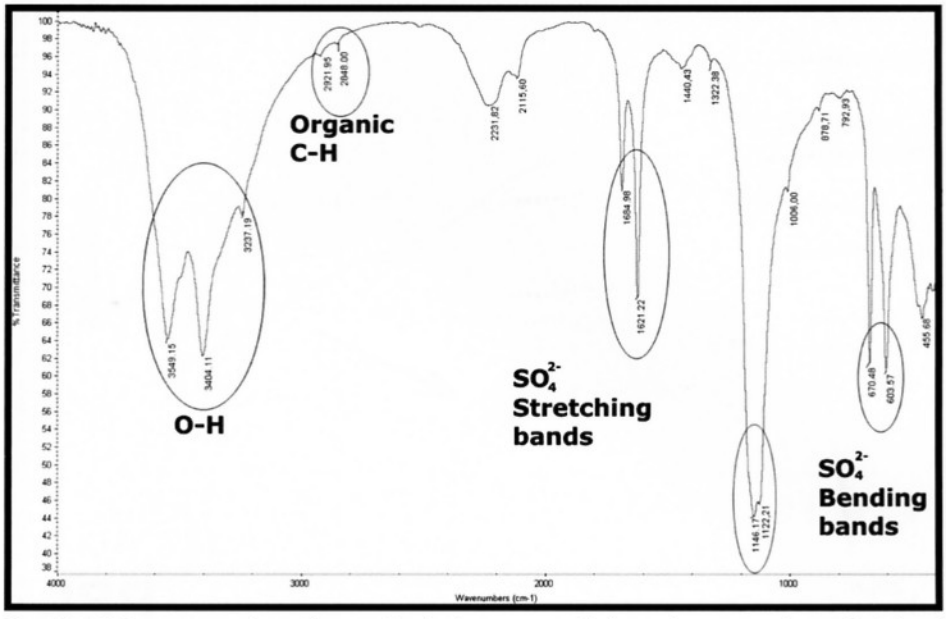

Fig. 10: FTIR spectrum of a yellow and red pigment sample from the apse arch, north side, of the S. Basilio Church at Mustafapaşha. Gypsum and organic material bands are put in evidence.

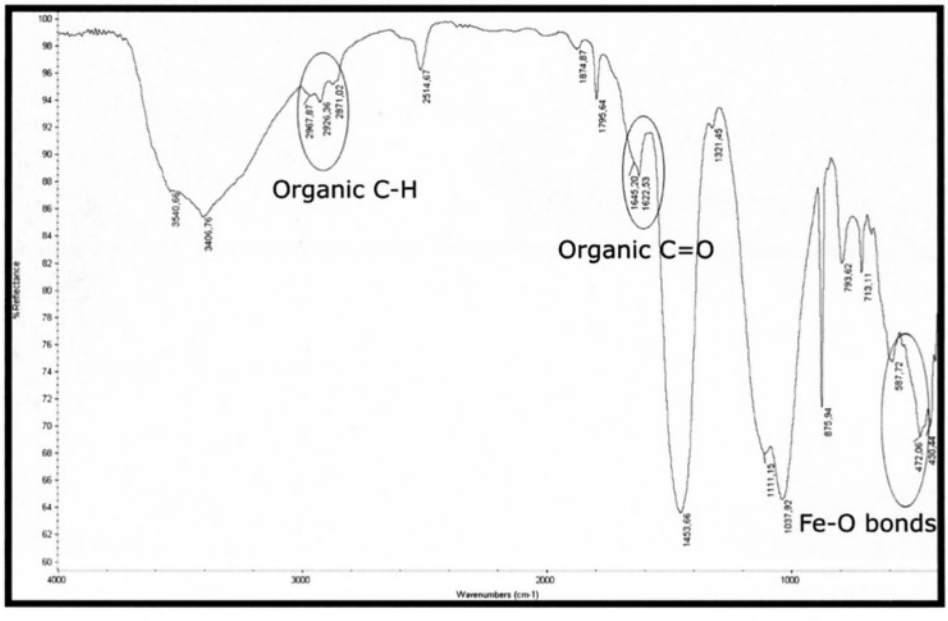

Fig. 11: FTIR spectrum of a red pigment sample from the apse, north side of Hayvali Kilisesi. Organic material and iron oxide bands are put in evidence.

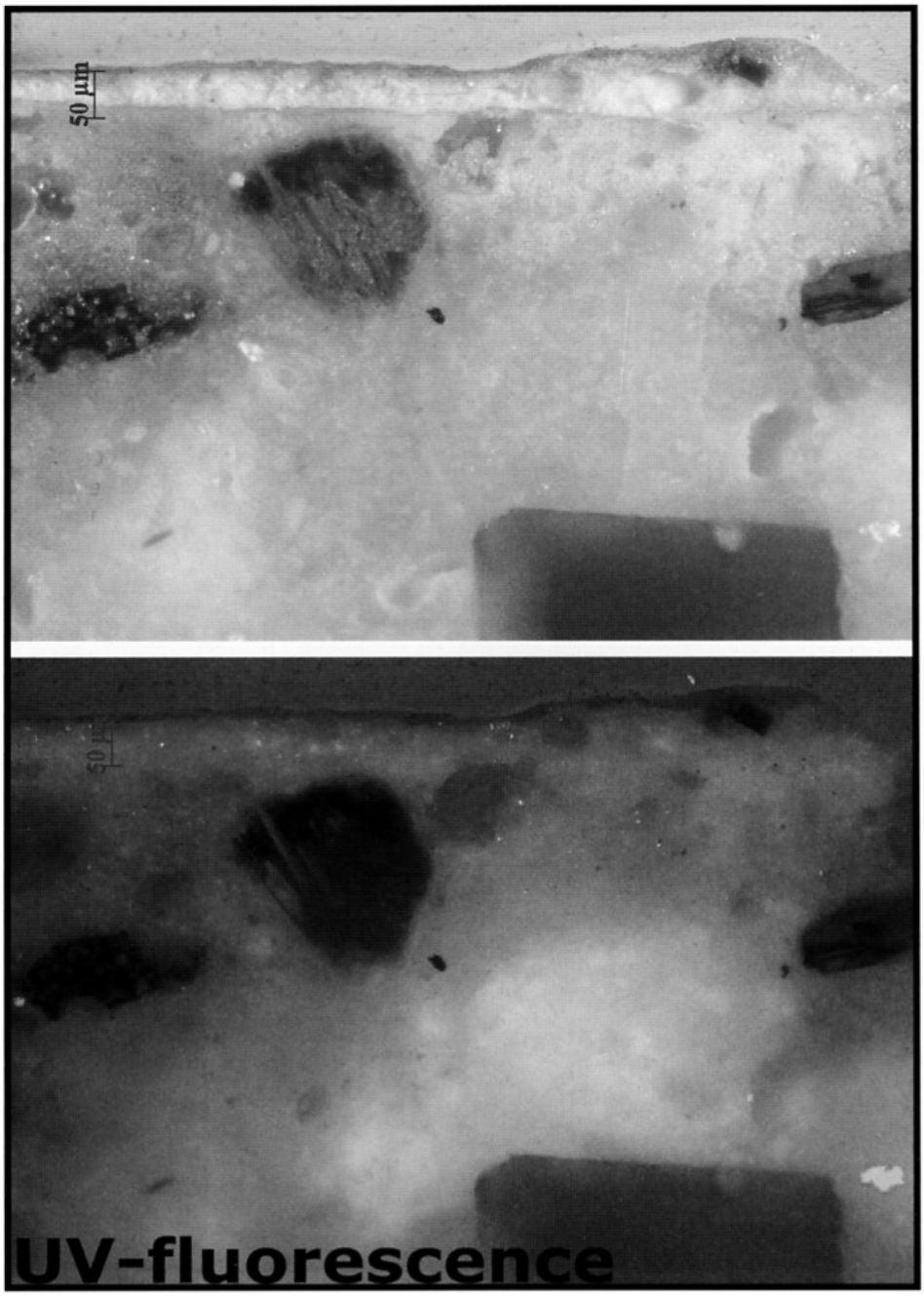

Fig. 12. Cross sections of a micro fragment from the apse, north side of Hayvalı Kilisesi. The green pigment is applied over a white layer that shows an orange UV-fluorescence.

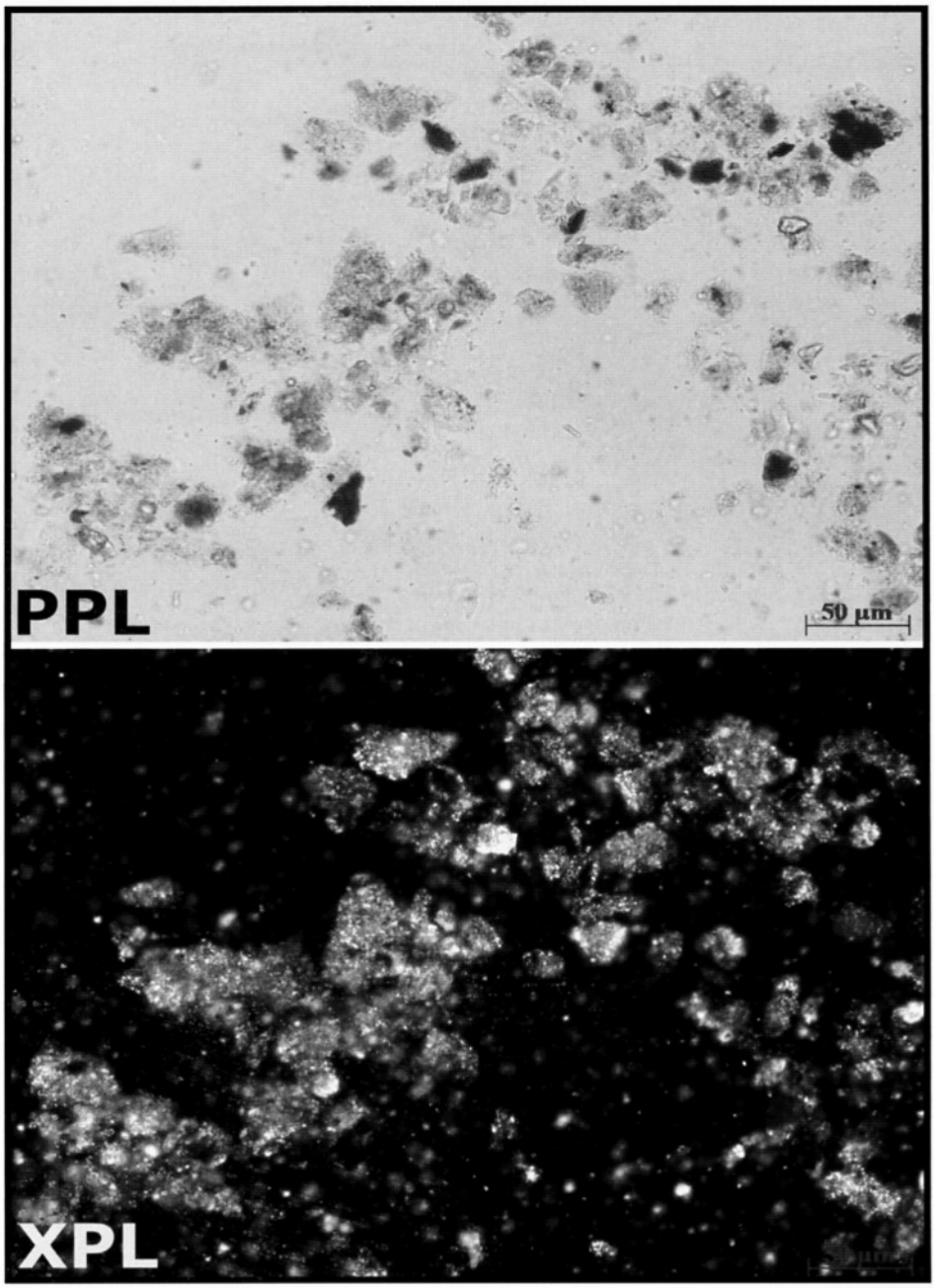

Fig. 13: Blue pigment from the decoration of the throne, S. Apostle Church, Narthex, Christ in Throne. Polarizing microscope observation, magnification 20x. Natural ultramarine, calcite and gypsum are visible.

Sites and number of the samples	Pigments	Other materials
Aunçilar Karsibecak Kilise (6)	Hematite, lead red, goethite	Calcite, gypsum, organic materials
Aunçilar Yusuf Kog Kilise (7)	Hematite, goethite, vegetable black	Gypsum, calcite
Çavusin Big pigeon-house (6)	Hematite, green earth, carbon black, ultramarine blue	Calcite, gypsum, proteinaceous materials
Çavusin S. John the Baptist (7)	Hematite, green earth, carbon black	Gypsum, calcite, proteinaceous materials
Cemil Archangel Monastery, Archangel Church (9)	Hematite, goethite, carbon black, ultramarine blue	Calcite, gypsum, proteinaceous materials
Cemil Archangel Monastery, S. Stephen Church (8)	Hematite, goethite, carbon black	Calcite, gypsum, organic materials
Güllü dere Ayvali Kilise nr 4 (8)	Hematite, goethite, carbon black	Limonite, gypsum, calcite
Güllü dere Church nr 5, Süslü Kilise (4)	Green earth	Gypsum, calcite
Kizil Çukur Haçli Kilise (13)	Hematite, lead red, goethite, green earth, vegetable black	Calcite, gypsum, organic dye, limonite
Kizil Çukur SS. Joachim and Anna (15)	Hematite, lead red, goethite, green earth, vegetable black	Calcite, gypsum, proteinaceous materials
Kizil Çukur Uzümlü (4)	Hematite, goethite	Gypsum, calcite
Şahinefendi Forty Martyrs Church (60)	Hematite, goethite, green earth, vegetable black, carbon black, lead yellow and red, cinnabar, organic dye	Calcite, gypsum, proteinaceous materials, tuffaceous rock fragments, anhydrite, magnetite
Soğanli Karabas (5)	Hematite, green earth	Gypsum, calcite
Ürgup Pancarlik Kilise (5)	Green earth	Organic materials, gypsum, calcite
Ali Reis Kilise, Orthaisar (4)	Hematite, goethite, vegetable black, probably red lead and cinnabar, lead based yellow pigments	gypsum, calcite,, organic materials, probably also restoration materials
Cambaszli Kilise, Orthaisar (4)	Hematite, goethite, vegetable black, probably red lead	gypsum, calcite, restoration materials
Hayvali Church (7)	Hematite, goethite, vegetable black, probably cinnabar, red lead, green earth	Gypsum, calcite, organic materials
Mustafapaşa, S. Basilio (5)	Hematite, goethite, vegetable black, probably red lead and cinnabar, lead based yellow pigments	Gypsum (abundant), calcite, organic materials
S. Apostles (1)	Natural ultramarine blue	Calcite, gypsum, organic materials

Fig. 14: Table of the overall results from the analysis of the samples of 2006-2008 campaigns.

UNIVERSITÀ Tuscia

LABORATORY OF DIAGNOSTICS FOR CONSERVATION AND RESTORATION "MICHELE CORDARO"

Card nr: 18-07 **Site**: ŞAHINEFENDI, Fourty Martyrs Church

Mark: SCQM18-07

Sampling nr: 18-07 **Date**: 20-09-07

Sample Nr 18

Place of sampling: south apse

Point of sampling: red frame, right side BI3 of the arch, third circle

Kind of material: micro fragment

Sampling description: mortar, pigment and black layer

Aim of the sampling: materials characterization

***In situ* observations:**

Photo nr.

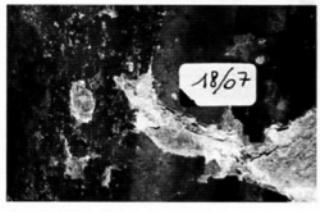

Figure 1: point of sampling

Sample at the stereo microscope

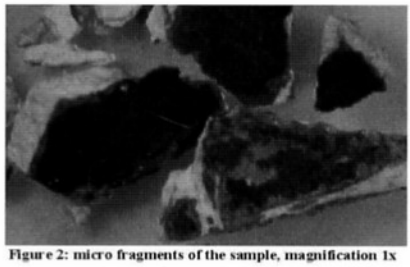

Figure 2: micro fragments of the sample, magnification 1x

Description of the micro sample

The sample is characterized by micro fragments (about 2,5 mm) constituted by the plaster mortar and two pictorial layers: yellow and brown.

Fig. 15: First page of the card used for the database of materials and techniques.