# THE WALL PAINTINGS OF THE CRYPT OF THE MEDIEVAL CHURCH OF SAINT ANDREW IN VITERBO (ITALY): TECHNICAL EXAMINATION AND STATE OF PRESERVATION

#### FABIO CASTRO1, CLAUDIO FALCUCCI2, CLAUDIA PELOSI1\*

<sup>1</sup> Faculty of Conservation of Cultural Heritage, Tuscia University Viterbo (Italy) <sup>2</sup> M.I.D.A. Metodologie d'Indagine per la Diagnostica Artistica, Roma (Italy)

\* Corresponding author: Claudia Pelosi, Department of Cultural Heritage. Largo dell'Università 01100 Viterbo, Italy. email: pelosi@unitus.it

#### Abstract

The wall paintings of the crypt of the church of Saint Andrew in Viterbo (Italy) date back to the 13th century. The bad state of preservation and the lack of many areas of the scenes make difficult a clear interpretation of the paintings and therefore a precise historical placing inside the 13th century. Besides an extensive analysis of the execution techniques and of the constitutive materials has never been undertaken. So the aim of this research has been to characterize the constitutive materials and the execution techniques of the wall paintings in order to provide a valid aid to the historical and artistic interpretation of the iconography and to evaluate the state of preservation of the paintings related to the environment. The wall paintings have been studied by means of non invasive methodologies of analysis and through laboratory techniques. The in situ investigations have been carried out by ultraviolet (UV) fluorescence and false colour infrared (IRC) photography, reflectance spectrophotometry, video microscope acquisitions, XRF spectrometry. These preliminary investigations have been useful to chose the sampling points for the laboratory analysis. The micro samples were examined through FTIR spectrometry and polarizing microscope observation of the pigment powders and of the cross sections. The pigments employed for the wall paintings are: red and yellow ochre, calcium carbonate white, lead based pigments probable red lead, green earth, vegetable black. They have been applied by a lime technique. The photographic campaign and the technical examination of the wall paintings also put in evidence the presence of surface damages. In particular, the abundant superficial salt deposits are the result of the use of unsuitable restorations materials in previous interventions. The environmental conditions (temperature and relative humidity) were registered by means of a digital data logger. During the months of October, November, and December 2009 the RH% values exhibit high average values, from 71 to 83%. The lowest RH% value (43%) has been registered on the fifteen of October, the highest one (86%) has been measured on the thirty-one of December. We believe that this study to be necessary for the future preservation and conservation of these interesting medieval wall paintings.

Keywords: medieval wall paintings, conservation, diagnostics, non destructive analysis

1. Introduction: description of the wall paintings and aims of the research

The wall paintings of the crypt of Saint Andrew's church in Viterbo are important evidences of the medieval paintings in Alto Lazio territory. The crypt dates back to the 12<sup>th</sup> century and some architectural elements may possible to assess that a gothic – cistercian style is present [1]. Wars, natural events, like earthquake in 1971, and the lack of ordinary maintenance seriously damaged the wall paintings of the crypt and today only some fragments survive (fig.1). So the crypt of Saint Andrew becomes an extraordinary evidence to study and to preserve.

The wall paintings of the crypt date back to the 13<sup>th</sup> century, but the bad state of preservation and the lack of many areas of the scenes make difficult a clear interpretation of the paintings and therefore a precise historical placing inside the 13<sup>th</sup> century. Many art historians were interested in these wall paintings: Scriattoli [2], Van Marle [3], Signorelli [4-5], Matthie [6], Parlato and Romano [7], Piferi [8]. They suggest different dating for the paintings ranging from the beginning of the 13<sup>th</sup> to the end of the same century (about 1281).

The map of the crypt with the number and the description of the scenes is reported in fig. 2. The map and the description of the scenes are taken from [1].

The crypt undertook some conservation interventions in 1902, 1958 and 1982. The first two interventions concerned only the architectural elements, whereas the 1982 intervention involved the wall paintings. On that occasion the wall paintings appeared fragmentary and covered up by a white layer of salts. They were consolidated, cleaned and some little reintegration have been carried out by means of water colours. All the conservation reports have been examined to obtain information about the used materials (Paraloid, Primal, calcium caseinate and vinyl polymers). It is important to stress that at the end of the conservation intervention the work director underlined the necessity of a year's maintenance to the salt formation. But this recommendation failed to apply and today the wall paintings are in danger of disappearing.

Therefore the aim of this work has been to carefully examine these wall paintings and to evaluate their environment in order to propose a possible solution to the conservative problems.

Concerning this the following steps have been undertaken:

- historical and archive documentation, supported by a detailed photographic campaign carried out by means of visible light, infrared and ultraviolet fluorescence photography;

- in situ investigation by means of non-destructive techniques (video microscope acquisitions, colorimetric measurements and XRF analysis);
- in situ monitoring of the micro climate conditions (relative humidity and temperature);
- sampling analysis carried out through laboratory techniques (FTIR spectrometry and polarizing microscope examination).

The characterization of the constitutive materials and of the execution techniques of the wall paintings can provide a possible aid to the historical and artistic interpretation of the iconography and the evaluation of the state of preservation related to the environment. This work would like to draw the attention to the need for a intervention on these wall paintings that like many other ones have been restored without considering the microclimate conditions and without an ordinary maintenance. For these reasons this work of art runs the risk of disappearing.



**Fig. 1.** A scene of the wall paintings (*Eucharistic lamb*, on the central apse of the north-west wall). The only survived evangelist symbols are the eagle and the bull head. The eagle holds the Gospel with the left claw.

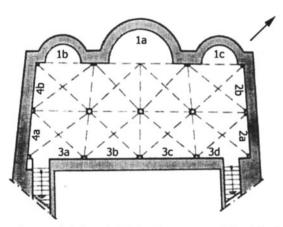


Fig. 2. Map of the crypt. The numbers and letters indicate the apses and the blind arches of the crypt walls with the following scenes: 1a - the *Eucharistic lamb*, two heads with haloes and a probable figure seated in throne; 1b - the half-length image of Christ, a three line inscription, three lambs and a horse hoof (probably the first episode of the *Genesis*); 1c - a bearded face with halo (Saint Peter); 2a - probably *Saint Peter martyrdom*; 2b - only a female ankle and foot; 3a - two female figures and other elements; 3b - an inscription referred to the purchasers and *Elisabeth Visitation to the Virgin*; 3c - The *Trip to Bethlehem*, probably the *Nativity*, the *Apparition of the star of the east* and probably the *Magi Adoration*; 3d - a figure seated in throne; 4a - probably *Saint Paul beheading*; 4b - some fragments representing three figures.

#### 2. Experimental section

#### 2.1. Non destructive analysis

The in situ investigations have been carried out by ultraviolet (UV) fluorescence and false colour infrared (IRC) photography, video microscope acquisitions, reflectance spectrophotometry, thermo hygrometric measurements and XRF spectrometry.

UV fluorescence photographs have been taken using a Nikon F70 camera and 2x160 Watt Philips MLW UV lamps positioned at 45° as regards the surface to be examined, on a Fujicolour Pro 160 C daylight colour film. The IRC photographs have been taken with a Nikon camera F3 on Kodak Ektachrome Infrared film. The illuminating system was made up of 2x250 Watt High component IR Photolyte lamps.

The images acquisitions have been realized through a portable video microscope Keyence directly connected to a portable computer through a graphic card. The spectrocolorimetric analyses have been performed by means a reflectance spectrocolorimeter X-Rite CA22 model with a spot area of 4 mm in diameter and 45°/0° geometry. The

measurements were taken according to the CIE 1976 method, with a 10nm step of measurement using the standard illumination D65/10°. The results are reported as L\*a\*b\* colour space.

XRF analysis have been performed through a portable X-Ray fluorescence spectrometer equipped with an X-ray generator (5-50 kV) and a Si-PIN (resolution 155 eV at 5.9 keV) detector.

Thermo-hygrometric measurements have been realized by means of a Testo 177-H1 digital datalogger. Temperature, relative humidity and dew point values have been collecting every hour. The thermo hygrometric measurements are still in progress.

These preliminary investigations have been useful to chose the sampling points for the laboratory analysis.

#### 2.2. Sampling analysis

Pigment powders, mounted in Canada balsam, and cross sections of mortars, embedded in polyester resin, were examined with a Zeiss Axioskop polarizing microscope at 2.5-40x magnification in incident and transmitted visible and UV lights. Photomicrographs were taken with the digital Zeiss AxioCam MR.

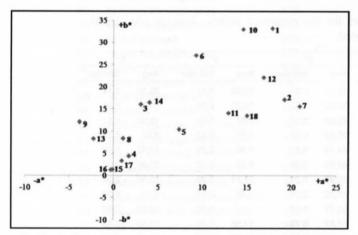
FTIR (Fourier Transform Infrared) and μFTIR analyses were performed by a Nicolet Avatar 360 spectrophotometer equipped with a DTGS detector and connected to a Centaurμs microscope equipped with a MCT detector. The spectra were collected in diffuse reflection modality. For each spectrum 128 consecutive scans were recorded with a resolution of 4 cm<sup>-1</sup>. As background, the spectrum of the KBr powder was used.

Soluble salts have been analyzed through quantitative spectrophotometry in the visible region employing a Merck Spectroquant® system.





Fig. 3. Visible and UV fluorescence photographs of the Apparition of the star of the east scene.



**Fig. 4.** a\*b\* chromaticity diagram with the measured points. For the description of the points see table 2.

**Table 1.** Comparison between visible, UV fluorescence and IR false colours of the eagle scene and hypothesis about pigment identification.

| Visible colour                         | UV fluorescence<br>colour | Infrared false color | Material                |
|--|---------------------------|----------------------|-------------------------|
| Yellow: halo,<br>wings, plumage        | Yellow-brown              | Light yellow-orange  | Yellow ochre            |
| Red: book and halo circle              | Deep red                  | Yellow-brown         | Red ochre               |
| White: halo circle,<br>wings, beak tip | Whitish and yellow        | White                | Calcium carbonate white |
| Plaster                                | Violet                    | Grey                 | No painted plaster      |

3. Results ar

### 3.1 False colour infrared photography (IRC)

Owing to the characteristic absorption of some pigments in the infrared region of the electromagnetic spectrum in many cases pigment identification is possible through IRC technique. The results for eagle in the central nave of the north-west wall are summed up in table 1. The comparison of these results with laboratory samples and literature data allowed to suppose pigment composition [9]. We can hypothesize the presence of yellow ochre in the haloes and in the eagle wings. This pigments appear light yellow in IRC. The red areas exhibit a yellow-orange colour in IRC indicating the presence of haematite, but probably also of other red pigments. White and black areas show the same colour in visible and IRC. Other yellow, red, black and white areas of the wall paintings give similar response to IRC technique, compared to that obtained for the central nave. Green backgrounds appear light blue to IRC suggesting the presence of green earth.

#### 3.2 Ultra violet fluorescence photography

This photographic technique has been very useful to detect surface damages and the characteristic fluorescence of some pigments that allows to hypothesize their composition [10].

In particular the detected damage has been:

- surface salt deposits caused by the use of cement and gypsum during previous conservation intervention before 1982.
- Extended flaking and detachments of the colour layers and of the mortars caused by the high relative humidity of the environment.
- Extended biological attack favoured by the presence of organic materials on the wall paintings (especially the calcium caseinate used in 1982 restoration intervention) and by the high RH% values.

Moreover, UV fluorescence photography put in evidence some details that today are no more visible. In the third blind arch of the south-east wall four episodes of the New Testament are represented, separated by brown frames. In the upper side of the wall the apparition of the star of the east and the Magi Adoration are represented. The Magi names have been put in evidence by means of UV fluorescence photography (fig. 3).

As regards the pigment identification by means of the examination of their UV fluorescence the following observations could be reported:

- red ochre, deep red fluorescence, identified in the frames of the scenes, in the outlines of the haloes and in some of the garments;
- yellow ochre, yellow-brown fluorescence, identified in the haloes, in the eagle plumage and in the book frame;
- red lead, orange fluorescence, identified in the of the Magi's garments, in the outline of the Christ image and in some frames of the scenes.

The white areas appear white under UV lighting or yellowish as in the inscription background in the left apse of the north-west wall. Probably the yellow colour is due to the presence of a diffuse biological attack.

| <b>Table 2</b> . L*a*b* | colour space  | values for th | e measured | points. | Average | (Avg)      | and |
|-------------------------|---------------|---------------|------------|---------|---------|------------|-----|
| standard deviation      | (Std dev) are | reported.     |            |         |         | 0000 00000 |     |

| Point of measurement                              | L*    |         | a*    |         | b*    |         |
|---|-------|---------|-------|---------|-------|---------|
| Posit of Insestrement                             | Avg   | Std dev | Avg   | Std dev | Avg   | Std dev |
| Yellow of the eagle halo, nr.1                    | 51,89 | 0,84    | 17,83 | 0,13    | 33,16 | 0,17    |
| Red outline of the eagle halo, nr.2               | 37,53 | 1,22    | 19,22 | 0,94    | 17,02 | 0,03    |
| White outline of the eagle halo, nr.3             | 78,20 | 0,33    | 3,07  | 0,05    | 15,94 | 0,17    |
| Black outline of the eagle wings, nr.4            | 30,91 | 0,41    | 1,75  | 0,23    | 4,37  | 0,17    |
| Brown of the eagle wings, nr. 5                   | 34,74 | 0,59    | 7,36  | 0,26    | 10,37 | 0,20    |
| Yellow of the eagle plumage, nr.6                 | 62,93 | 0,49    | 9,29  | 0.08    | 27,06 | 0,06    |
| Red of the book, nr.7                             | 33,23 | 0,24    | 20,91 | 0,29    | 15,55 | 0,26    |
| White of the book background, nr.8                | 82,22 | 2,96    | 1,10  | 0,11    | 8,37  | 0,29    |
| Green of the lamb outline, nr.9                   | 51,71 | 0,67    | -3,82 | 0.40    | 12,03 | 0,82    |
| Yellow of the eagle wings, nr.10                  | 57,87 | 0,77    | 14,58 | 0,16    | 33,00 | 0,65    |
| Red-brown of the eagle wings, nr.11               | 35,87 | 0,09    | 12,95 | 0,08    | 14,05 | 0,36    |
| Yellow-brown of the background, nr.12             | 46,63 | 0,15    | 16,87 | 0,14    | 22,06 | 0,43    |
| Green of the background in the left apse, nr.13   | 42,38 | 0,46    | -2,23 | 0,27    | 8,31  | 0,93    |
| White-pink of the Christ cheek, nr.14             | 65,12 | 0,47    | 4,06  | 0,27    | 16,39 | 0,60    |
| Black of the Christ mandorla, nr.15               | 30,61 | 0,31    | -0,08 | 0,02    | 1,38  | 0,05    |
| Black of the Christ mandorfa, nr.16               | 37,97 | 3,07    | -0,28 | 0,07    | 1,26  | 0,30    |
| Grey of the background in the central apse, nr.17 | 53,07 | 1,59    | 0,94  | 0,50    | 3,33  | 0,48    |
| Red of the mandorla outline, nr.18                | 33,73 | 0,12    | 15,02 | 0.07    | 13,42 | 0,03    |

#### 3.3 Reflectance spectrophotometry

Colorimetric parameters according the CIELAB colour space are reported in table 2. Moreover the a\*b\* chromaticity diagram is reported in order to clearly observe the colour analogies and differences between the

examined areas (fig. 4). For each measured area the reflectance spectrum was examined and compared with literature data and laboratory samples (data not reported). The a\*b\* chromaticity diagram shows that the yellow area of the halo and of the wing of the eagle (points 1 and 10) are similar. The L\*a\*b\* data and the reflectance spectrum of these colours compared with literature references suggest the presence of raw Sienna, a yellow iron hydroxide pigment containing also manganese oxide, clay and quartz [11]. Another yellow area has been measured on the eagle's neck (point 6). This surface exhibit a lower red component probably for the presence of more iron hydroxides and less haematite. Red and brown areas show more dispersions of a\* and b\* parameters. This suggests a greater variability of the used materials. Comparing the data for red and brown areas with literature references [11] no clear correspondence has been found. It must be stressed that the colour of the iron oxide pigments is influenced by many factors like the particle size and shape, the chemical composition, the temperature of treatment and also by the proportion and nature of minerals associated with the pigment. So it is difficult to find a close analogy with literature data. Nevertheless it could be possible to make hypothesis on the typology of materials. The brown areas of the wall paintings of the crypt show analogies with the raw and burnt umbers. The red areas are probably constituted by pigment mixtures because the colorimetric parameters don't match the reference data.

Green areas (points 9 and 13) exhibit similar colorimetric parameters, point 9 has a higher yellow component probably due to the influence of the yellow-red background visible in the video microscope acquisitions of this point. The colorimetric data suggest the presence of a green earth with a dark yellowish hue, the dominant wavelength was in fact at about 560-570 nm [12].

White areas (points 3 and 14) are quite similar whereas point 8 exhibits different colorimetric parameters. A comparison with literature data [13] and with the other analysis carried out on the wall paintings suggest the presence of calcium carbonate. Probably in the book (point 8) the colour is not influenced by the background whereas in the other two points the yellow of the halo and the Christ flesh respectively affect the white colour.

The colour measurements in the black area suggest the presence of two different pigment typologies. Point 4 and 17 are similar and exhibit a little difference with point 15 and 16 measured on the Christ *mandorla*. These two last points show a green component. Point 4 colour is influenced by the yellow of the eagle wings that was applied before the black colour. Point 17 colour appears grey and it has been obtained by a mixture of white and black. As regards the black area of the *mandorla* a comparison with literature data [14] and the other analysis carried out on the wall paintings suggest the presence of vine black as pigment.

Table 3. Fluorescence intensities for the detected elements (cps).

| Point | Colour                              | Ca  | Mn | Fe  | Rb | Sr  | Zr  | Pb |
|-------|-------------------------------------|-----|----|-----|----|-----|-----|----|
| 01    | Yellow of the eagle wing            | 227 |    | 275 | 54 | 222 | 82  |    |
| 02    | Brown of the eagle wing             | 218 |    | 288 | 69 | 219 | 82  |    |
| 03    | Red of the eagle halo               | 235 |    | 318 | 57 | 242 | 130 | 16 |
| 04    | Red of the book                     | 205 |    | 561 | 40 | 329 | 72  | 65 |
| 05    | Red of the eagle frame              | 233 |    | 397 | 58 | 249 | 87  |    |
| 06    | Yellow of the eagle halo            | 210 |    | 453 | 56 | 257 | 76  | 14 |
| 07    | White of the book backgroud         | 285 |    | 65  | 59 | 219 | 85  |    |
| 80    | White of the eagle wing             | 265 |    | 154 | 60 | 209 | 91  |    |
| 09    | Black of the eagle wing             | 188 |    | 121 | 58 | 276 | 85  |    |
| 10    | Red-orange of the background        | 189 |    | 573 | 83 | 210 | 78  | 20 |
| 11    | Green of the eagle background       | 218 | 32 | 224 | 83 | 227 | 82  | 18 |
| 12    | Black of the Christ mandorla        | 164 |    | 214 | 78 | 234 | 91  |    |
| 13    | Black of the Christ mandorla 2      | 219 |    | 183 | 70 | 200 | 110 | 30 |
| 14    | Red of the mandorla frame           | 172 |    | 582 | 59 | 236 | 60  | 92 |
| 15    | White of the inscription background | 490 |    | 32  | 61 | 217 |     |    |
| 16    | Green of the lamb background        | 392 |    | 127 | 48 | 268 | 104 |    |
| 17    | Red of a Magus garment              | 247 |    | 170 | 30 | 250 | 98  | 44 |
| 18    | Green of the Magi background        | 280 |    | 80  | 70 | 325 | 79  |    |
| 19    | Yellow of a Magus garment           | 337 |    | 295 | 41 | 322 | 78  | 21 |
| 20    | Red of the Magi scene frame         | 372 |    | 189 | 56 | 321 | 76  |    |

#### 3.4 Video microscope acquisitions

Video microscope acquisitions are useful to obtain a high magnification of the painted surfaces so that mixtures of pigments, alterations, surface abrasions and other particulars can be put in evidence in a totally non invasive modality. Thirty acquisitions were taken at four magnifications (25x, 50x, 100x and 175x). The following observations have been possible:

- some colour lacks of the painted surfaces (fig. 5A);
- the presence of a transparent material over the painted surfaces (fig. 5B). This material has been identified as the acrylic resin used on the occasion of the conservation intervention in 1982. In particular the conservation report specifies the use of Paraloid B72;
- many colour superimpositions. For example, in the haloes the outlines have been painted over the yellow background (fig. 5C);
- soluble salts clearly visible on the wall painting surfaces, especially in the lower parts of the walls and in the south-east wall (fig. 5D).

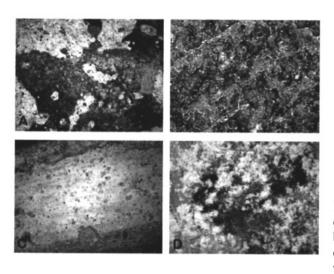
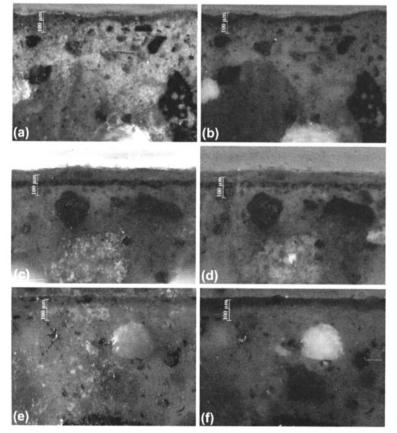


Fig. 5. Video microscope acquisitions of different areas. A) eagle beak; B) green background, left apse; C) eagle halo outline; D) a figure eye in the south-west wall.



**Fig. 6.** Cross sections of micro fragments of the samples SA1 (a, b), SA3 (c, d) and SA8 (e, f). (a), (c) and (e) reflected light; (b), (d) and (f) UV fluorescence. For the description of the samples see table 4.

#### 3.5 XRF analysis

The results of XRF analysis are reported in table 3. The values in the table are the total amounts of detected photons for each determined element during the acquisition time.

Rubidium, zirconium and a fraction of the detected iron can be referred to the *pozzolana* used as aggregate in the mortars. Calcium and strontium can be referred to the calcium compounds used as binder in the same mortars. The increase of the XRF counts for this element in the white areas confirms the use of a calcium carbonate pigment to obtain this colour. The black areas were realized by a carbon based pigment that cannot be detected by XRF analysis.

The yellow, orange, green and red areas have been obtained by iron based pigments: yellow and red ochre, green earth. A not negligible amount of lead has been detected in three of the six analysed red points. This result suggests the use of a minium/red ochre mixture or of two different kinds of red ochre, one of which naturally contains lead impurities.

Table 4. Results of FTIR spectrometry analysis. Samples have been marked with alphanumerics (SA for Saint Andrew) followed by a progressive

| number.   | Main bands (cm <sup>4</sup> )  | Results  |
|---|--|--|
| SA1, red-brown of the eagle wing                                | 2982.9, 2872.1, 2511.7, 1794.4, 1451.2, 875.1, 756.2, 712.5; 2948.4, 1730.4, 1033.1; 3542.8, 3401.9, 1631.2, 1143.8, 1116.3  | Calcile, acrylic resin,<br>gypsum, iron oxides                         |
| SA2, red of the eagle halo<br>outline                           | 2962.6, 2875.2, 2511.8, 1794.7, 1447.2, 1385.0, 875.3, 762.7, 712.4; 2951.4, 1728.4, 1030.7; 541.1, 464.0; 1622.4, 1140.7, 1110.3; 3619.0; 3310.0, 1652.8                              | Calcite, acrylic resin,<br>iron oxides, gypsum,<br>silicates, proteins |
| SA3, green of the background<br>in the Magi scene               | 2978.8, 2669.1, 2511.5, 1794.6, 1438.4, 1384.2, 876.2, 712.4; 3535.6, 3399.7, 2237.4, 2119.2, 1682.8, 1621.8, 1143.8, 1117.1, 672.3, 602.4, 462.3; 1037.1; 3244.0, 2924.0              | Calcite, gypsum, iron<br>oxides silicates,<br>organic compounds        |
| SA4, red of the Christ<br>mandarle outline                      | 2961.9, 2511.9, 1796.1, 1442.6, 875.0, 760.7, 710.9; 2925.8, 2853.9, 1734.4, 1029.8; 533.2, 468.2; 3616.9, 1029.8  | Calcite, acrylic resin,<br>iron oxides, silicates                      |
| SA5, black area of the Christ<br>mandorla                       | 2983.5, 2511.9, 1794.1, 1447.7, 875.1, 756.5, 712.2; 2948.4, 1730.7, 1235.2, 1028.4; 543.3, 473.2; 3415.3, 1631.5, 1143.8; 3609.8, 1095.0, 1028.4                                      | Calcite, acrylic resin,<br>iron oxides, gypsum,<br>silicates           |
| SA6, grey-black area of the<br>Christ mandorla                  | 2983.3, 2513.7, 1794.2, 1451.1, 875.4, 762.7, 713.6; 2948.4, 2924.0, 1734.4, 1235.2, 1031.1; 3536.7, 3407.8, 1628.1, 1110.3, 671.3, 601.2, 452.3                                       | Calcite, acrylic resin, gypsum   |
| SA7, red and black of a<br>garment, south-east wall, II<br>arch | 2978.8, 2872.1, 2511.8, 1794.8, 1442.6, 1384.4, 875.4, 823.4, 712.3; 3539.7, 3401.0, 2233.6, 2113.1, 1682.7, 1622.2, 1146.8, 1116.5, 671.1, 602.4, 463.6; 540.2, 463.6; 1729.0; 1039.5 | Calcite, gypsum, iron<br>oxides, acrylic resin,<br>silicates           |
| SA8, red and yellow area in<br>the sud-eastwall, II layer       | 2981.9, 2872.1, 2512.5, 1795.0, 1461.4, 875.6, 791.8, 712.5; 540.2, 462.0; 3419.0, 1103.3, 462.0   | Calcille, iron oxides, gypsum  |
| SA9, green background of the<br>lamb in the central apse        | 2963.6, 2672.1, 2512.4, 1794.3, 1449.3, 675.2, 712.8; 2948.4, 2902.6, 1729.7, 1031.3; 3545.8, 3403.3, 1680.3, 1623.1, 1146.8, 1115.2, 672.2, 604.2, 452.3                              | Calcile, acrylic resin,<br>gypsum, iron oxides                         |
| SA10, white background of<br>the Gospel                         | 2978.8, 2672.1, 2512.3, 1794.5, 1462.2, 675.4, 712.7; 3542.8, 3404.9, 1683.3, 1623.4, 1143.8, 1116.3, 672.6, 601.2, 436.6; 543.3, 470.1; 1037.4; 1723.0                                | Calcite, gypsum, iron<br>oxides, silicates, acrylic<br>resin           |
| SA11 white of the eagle halo<br>outline                         | 2965.3, 2872.1, 2511.5, 1794.7, 1461.5, 874.9, 712.3; 3411.2, 1683.3, 1624.7, 1146.8, 1113.3, 670.0, 601.2, 464.2; 543.3, 464.2; 1032.6; 2948.4, 1731.8, 1032.6                        | Calcille, gypsum, iron<br>oxides, silicates, acrylic<br>resin          |
| SA12 white beckground of the<br>inscription in the left apse    | 2981.9, 2872.1, 2512.5, 1794.8, 1459.2, 875.9, 712.3; 3436.0, 1683.3, 1629.8, 1149.9, 1106.0, 665.2, 604.2, 431.8, 537.2, 467.1; 1729.9  | Calcite, gypsum, acrylic<br>resin                                      |

**Table 5.** Result of the polarizing microscope observation of pigment powders.

| Pigment sample   | Observed materials  |
|--|---|
| SA1, red-brown and yellow of the eagle wing                  | Red and yellow othre, calcile, many vegetable black particles few gypsum crystals, an organic resin                                   |
| SA2, red of the eagle halo outline                           | Red ochre, calcite, some vegetable black particles, few gypsum crystals, an organic resin   |
| SA3, green of the background in the<br>Magi scene            | Green earth, calcite, several vegetable black particles, gypsum, red ochre particles, an organic resin                                |
| SA4, red of the Christ mandorle outline                      | Red ochre, calcite, probably lead red, few vegetable black<br>particles, gypsum, an organic resin, proteins (blue UV<br>fluorescence) |
| SA5 and SA6, black area of the Christ mandorla               | Vegetable black, calcile, a lot of gypsum crystals, few red ochre particles, probably cinnabar, an organic resin                      |
| SA7, red and black of a garment, south-<br>eastwall, II arch | Red ochre very fine particles, calcite, a lot of gypsum crystals, vegetable black, an organic resin                                   |
| SA8, red and yellow area in the sud-east wall, Il layer      | Red and yellow ochre, calcile, very fine vegetable black particles, gypsum, a trasperent organic resin                                |
| SA9, green background of the lamb in<br>the central apse     | Green earth, calcite, a lot of vegetable black particles, gypsum, red ochre particles, an organic resin                               |
| SA10, white background of the Gospel                         | Calcite, gypsum, few red earth and vegetable black particles, proteins, an organic resin  |
| SA12 white background of the inscription in the left apse    | Calcile, gypsum, few vegetable black particles, proteins, an organic resin  |

**Table 6.** Relative humidity (RH%) and temperature (t °C) data for the three monitored months.

| Month    |     | Min  | Max  | Monthly average | Monthly<br>std dev |
|----------|-----|------|------|-----------------|--------------------|
| October  | RH% | 43,2 | 79,9 | 71,1            | 7,93               |
| October  | t°C | 15,6 | 20,6 | 17,9            | 1,74               |
| November | RH% | 76,5 | 84,3 | 80,7            | 2,26               |
|          | t°C | 14,0 | 16,3 | 14,7            | 0,50               |
| December | RH% | 75,0 | 86,0 | 82,6            | 1,71               |
|          | t°C | 10,3 | 14,5 | 12,1            | 1.17               |

#### 3.6 FTIR spectrometry

FTIR analysis results are reported in table 4. The measurements have been realized on the powders of the pigments taken off the wall paintings. Gypsum and an acrylic resin has been found in almost all of the examined samples. Calcium sulphate dihydrate is more abundant in the samples taken off from the lower parts of the walls and in the south-east wall. The presence of high quantities of gypsum is probably linked to its use as restoration material during the past conservation intervention before 1982. The high relative humidity of the crypt and especially its large variations has favoured the diffusion of gypsum and its surface deposition as salt efflorescence. FTIR analysis doesn't detect the presence of organic binders suggesting a fresco and/or a lime technique. The traces of organic compounds have to be referred to the calcium caseinate and to the Paraloid B72 employed in the conservation intervention in 1982.

#### 3.7 Soluble salts analysis

A sample of salt efflorescence has been analysed to detect the main ionic species. The main anion is sulphate (38.0 ppt) confirming the presence of gypsum. Other revealed ions are chloride (3.90 ppt); ammonium (2.38 ppt); potassium (3.60 ppt) and traces of nitrate and nitrite.

## 3.8 Polarizing microscope examination of pigments and mortars

Pigment powder observation under polarizing microscope allowed to confirm their composition and to detect the presence of mixtures and minor compounds. Table 5 summarizes the main results of the polarizing microscope observation of the pigments embedded in Canada balsam.

Cross sections of the mortars taken off the different wall paintings were examined through polarizing microscope in visible light and UV fluorescence (fig. 6). The mortars from the north-west wall are made of lime and sand with some hydraulic aggregates. The pictorial layer is not homogeneous and it is about 30  $\mu$ m micron meter thick. The pigments seem to be applied through a lime technique. Mortar samples from the south-east wall and that of the II layer in first arch of the same wall exhibit a similar composition: they are made of lime and few hydraulic aggregates. The pictorial layers appear more thick than that of the north-west wall (about 50-60 micron meter  $\mu$ m) and it has been applied by a lime technique. This interesting result confirm the hypothesis of the art historian Piferi who supposed that the scenes in the north-west wall were realized in the third decade of the 13<sup>th</sup> century whereas almost all the other ones should be referred to the end of the same century.

#### 3.9 Relative Humidity and Temperature data

The environmental conditions (temperature and relative humidity) have been registered by means of digital data logger. Maximum, minimum and monthly average values are reported in Table 6. The monthly standard deviation has also been calculated. During the last three months RH% exhibits high and increasing average values (71 % in October, 81% in November and 83% in December). The standard deviation is particularly high during October. On the contrary temperature values exhibit a clear decreasing trend. The crypt environment is clearly influenced by the external climate because no conditioning system is present. We are going to register the relative humidity and temperature values for at least one year in order to control the microclimate conditions in all the seasons. We hope this work could help to draw the attention to the wall paintings of the crypt of Saint Andrew and to save them before they disappear.

#### 4. Conclusions

The study of the thirteenth century wall paintings of the crypt of Saint Andrew in Viterbo allowed the characterization of the constitutive materials, the execution techniques and the state of preservation, pointing out the potentiality of the photographic documentation methods and of the non-destructive analysis. The technical examination of the mortars also confirmed the art historian hypothesis that two different pictorial phases are present. Firstly this work put in evidence the conservation problems of the wall paintings that mainly derive from the use of unsuitable restoration materials in an environment with high relative humidity values, without an ordinary maintenance. For instance, Paraloid B72 tends to become grey and to wrinkle in high RH% environments. We propose an immediate intervention in order to stop the damage advancing (especially plaster and colour layer detachments). Moreover it would be appropriate to install an air condition system to keep under control the microclimate parameters. At last a planned maintenance should be provided to avoid that these interesting paintings could disappear.

#### **AKNOWLEDGEMENTS**

The authors would like to thank Don Alfredo Cento, the parish priest of the church of Saint Andrew for having allowed the admission to the crypt. He is a very kind and helpful person.

#### References

- [1] Castro F. (2008) *Indagini diagnostiche sui dipinti murali della cripta di Sant'Andrea a Pianoscarano*, Thesis, Faculty of Conservation of Cultural Heritage, Tuscia University Viterbo (Italy), 218 p.
- [2] Scriattoli A. (1915-1920) Viterbo nei suoi monumenti, Stab. Ditta F.lli Capaccini, Roma, 470 p.
- [3] Van Marle R. (1923) The development of the Italian school of painting, vol. I, The Hague: Martinus Nijhoff, Netherland, 171-172 p.
- [4] Signorelli G. (1934) I più antichi pittori viterbesi, Bollettino Municipale, anno XIII, 4 p.
- [5] Signorelli M. (1964) Guida di Viterbo, Agnesotti, Viterbo, 114 p.
- [6] Matthie G. (1951) Note di pittura laziale nel Medioevo, Bollettino d'Arte 11, 112-118.
- [7] Parlato E., Romano S. (1992) Italia Romanica, Roma e il Lazio, vol. 13, Jaka Book, Milano, 307 p.
- [8] Piferi M.E. (2001) Affreschi romanici nel viterbese, Vecchiarelli, Roma, 70-78 p.
- [9] Castro F., Pelosi C. (2009) Study of Wall Paintings and Mosaics by means of Ultraviolet Fluorescence and False Colour Infrared Photography, in: Macchia A., Borrelli E., Campanella L. (Eds.), Proceedings of the International Meeting YOCOCU, Rome, November 24-25, 2008, Rome, 197-199 p.
- [10] Daniila S., Sotiropoulou S., Bikiaris D., Salpistis C., Karagiannis G., Chryssoulakis Y., Price B. A., Carlos J. H. (2000) *Panselinos' Byzantine wall paintings in The Protaton Church, Mount Athos, Greece: a technical examination*, Journal of Cultural Heritage 1, 91-110.
- [11] Helwig K. (2007) *Iron Oxide Pigments. Natural and Synthetic*, in Artists' Pigments A Handbook of Their History and Characteristics (Barbara H. Berrie, Ed.), National Gallery of Art, Washington, Archetype Publications, London, 39-109 p.
- [12] Grissom Carol A. (1986) *Green Earth*, in Artists' Pigments A Handbook of Their History and Characteristics (Robert L. Feller, Ed.), National Gallery of Art, Washington, 141-167 p.
- [13] Rutherford J., Kühn H., Chase W.T. (1993) *Lead White*, in Artists' Pigments A Handbook of Their History and Characteristics (Ashok Roy, Ed.), National Gallery of Art, Washington, 67-81 p.
- [14] Winter J., West FitzHugh E. (2007) *Pigments Based on Carbon*, in Artists' Pigments A Handbook of Their History and Characteristics (Barbara H. Berrie, Ed.), National Gallery of Art, Washington, Archetype Publications, London, 1-37 p.