

TECHNICAL PAPER

## FAR INFRARED SPECTROSCOPY IN THE FIELD OF CULTURAL HERITAGE

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**In the field of FTIR spectroscopy of heritage materials, the Far Infrared (FIR) region has been less investigated than the Mid Infrared (MIR) although it has some advantages, particularly in characterisation of inorganic compounds such as painting materials and corrosion products, which are not active in the MIR. Furthermore, FIR spectroscopy is a complementary technique to Raman spectroscopy in particular in the presence of fluorescence. In this study we have investigated the FIR region (600-90 cm<sup>-1</sup>) of eight inorganic standard pigments employed in art. The eight standard compounds are the preliminary results collected in order to build a larger FIR-database library. One case study is also presented.**

### 1 Introduction

MIR spectroscopy has been widely used in investigations of samples of works of art for instance paint samples,<sup>1-2</sup> parchment,<sup>3</sup> glass<sup>4-5</sup> and corrosion products.<sup>6</sup> However, MIR spectroscopy becomes less useful when investigating inorganic components such as oxides or sulphides, which are inactive in the MIR region. So far, Raman spectroscopy has been employed to overcome such limitations<sup>7-8</sup> and by means of Raman spectroscopy it is possible to observe heavy oxides and sulphides in paint samples. However, in the presence of organic compounds Raman spectra may be affected by fluorescence and several studies are being carried out to reduce this phenomenon by means of mathematical<sup>9</sup> or instrumental methods.<sup>10</sup>

FIR spectroscopy is used in different fields such as astrophysical,<sup>11</sup> cation exchange and interactions in ceramics<sup>12-13</sup> and lattice vibrations in the field of polymer crystallisation.<sup>14</sup> Recent studies reported the use of FIR spectroscopy to distinguish between different micas.<sup>15</sup> Studies from 1969 highlight its analytical potential for the investigation of minerals in the 200-50 cm<sup>-1</sup> region,<sup>16</sup> other studies discuss the assignment of external vibrations in liquid and solid phases.<sup>17</sup> However, only a few articles about FIR spectroscopy applied in the field of cultural heritage have been published<sup>16,18</sup> and for this reason

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the creation of a FIR library of artistic and corrosion materials is of utmost importance. In this paper we present the results obtained in transmission mode on a selection of eight pigments and on a real case study. The aim is to evaluate FIR spectroscopy performance for the detection of inorganic compound as a complementary technique to Raman and MIR spectroscopy.

## 2 Materials and Methods

### 2.1 Reference Pigments

All reference pigments have been examined by FIR spectroscopy. The composition and impurities of 9 standards are confirmed by Raman spectroscopy collected on a micro-Raman Labram with a 488 nm laser using 0.5-5 mW energy. Eight of the standard pigments were purchased from Kremer Pigmente.<sup>19</sup> One standard pigment, hematite ( $\text{Fe}_2\text{O}_3$ ) was purchased from Zecchi in Florence.<sup>20</sup> Also mineral samples of quartz and calcite have been investigated although not by Raman but by powder XRD, which confirms their purity. All the pigments are listed in Table 1.

### 2.2 Sampling

Samples were collected from the mural painting made by Giuseppe Milani in 1773-74, which covers the entire cupola in Abbazia del Monte (Cesena, Italy). Sample AM1 is a pale red and white sample taken from a dotted area of a cloud (Figure 1)

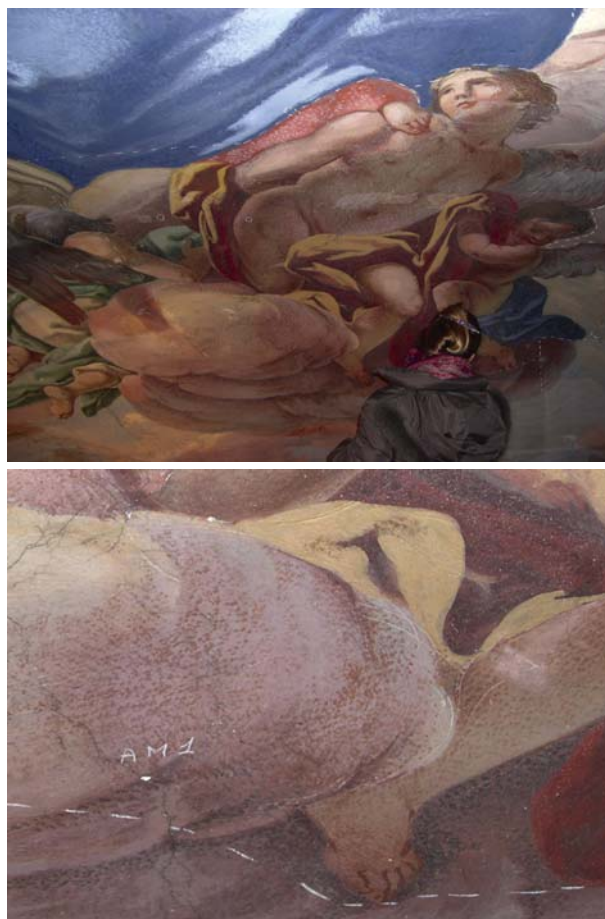


Figure 1a: Photograph of "Angel on a red cloud" which is part of a mural painting covering the Cupola and Figure 1b: near the sampling area AM1. The pictures were taken during recent restoration work of Abbazia del Monte in Cesena, Italy.

Pigment	Provenance	Chemical composition*	Raman identification
1 Bremer blue (synth. Azurite)	Kremer pigmente 10180	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ + Quartz ( $\text{SiO}_2$ )
2 Milori blue	Kremer pigmente 45200	$\text{FeNH}_4\text{Fe}(\text{CN})_6$	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14-16\text{H}_2\text{O}$ + small impurities Cuprite ( $\text{Cu}_2\text{O}$ ) and Hausmannite ( $\text{Mn}_3\text{O}_4$ )
3 Viridian green	Kremer pigmente 44250	$\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	$\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ + $\text{Cr}_2\text{O}_3$ + small impurity Calcite ( $\text{CaCO}_3$ )
4 Bavarian green earth	Kremer pigmente 11100	Al, K, Mg, Ca, Fe-silicates	Quartz ( $\text{SiO}_2$ ) + small amount of impurities: Hollandite ( $\text{BaMn}(\text{II})\text{Mn}(\text{IV})_7\text{O}_{16}$ ) + Anatase ( $\text{TiO}_2$ ) + Calcite ( $\text{CaCO}_3$ ) + Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ )
5 Lead tin yellow (type 1)	Kremer pigmente 10110	$\text{Pb}_2\text{SnO}_4$	Lead tin yellow ( $\text{Pb}_2\text{SnO}_4$ ) + cassiterite ( $\text{SnO}_2$ ) + massicot ( $\text{PbO}$ )
6 Barium yellow	Kremer pigmente 43940	$\text{BaCrO}_4$	Barium yellow ( $\text{BaCrO}_4$ )
7 Cinnabar	Kremer pigmente 10625	HgS	HgS + particle impurities: Quartz ( $\text{SiO}_2$ ) + Barium white ( $\text{BaSO}_4$ ) + Azurite ( $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ) + Phthalocyanine PG36 ( $\text{C}_{32}\text{Br}_6\text{Cl}_{10}\text{CuN}_8$ )
8 Terra di Siena (burnt)	Kremer pigmente 40450	Hematite ( $\text{Fe}_2\text{O}_3$ ), amorphous silica with impurities (1-10%) $\text{MnO}_2$ , alumina, $\text{CaCO}_3$	Hematite ( $\text{Fe}_2\text{O}_3$ ) + Quartz ( $\text{SiO}_2$ ) + Argentojarosite ( $\text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) + C (amorphous)
9 Hematite	Zecchi, Florence	$\text{Fe}_2\text{O}_3$	Hematite ( $\text{Fe}_2\text{O}_3$ ) + C (amorphous)
10 Quartz	Geological Museum, University of Bologna, Italy	$\text{SiO}_2$	No Raman, but powder XRD analysis confirms that the sample is pure. The mineral sample originates from Reggio Emilia, Italy.
11 Calcite	Geological Museum, University of Bologna, Italy	$\text{CaCO}_3$	No Raman, but powder XRD analysis confirms that the sample is pure. The mineral sample originates from Posso Raticosa, Bolivia.

Table 1: List of reference pigments and their chemical composition as reported by the supplier and as found by Raman analysis. \* as specified by the supplier.

beneath the Angel. Two PE pellets were made from this sampling. It was impossible when selecting the grains for pellet making to avoid white grains together with the red grains. AM1a was more red coloured than AM1b. Approximately 0.3-0.5 mg of sample was used for preparation of the PE pellets.

### 2.3 FIR Spectroscopy

The spectrometer used is a Thermo Nicolet Nexus 5700 using a solid-substrate™ beam splitter operating in the FIR region of 600-90  $\text{cm}^{-1}$ . A Parker/Balston Self-Contained Purge Gas Generator is attached, purging the spectrometer with dry air for minimizing interference bands generated from ambient moisture. The detector is a DTGS detector with a Polyethylene window used with a spectral resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.6329  $\text{cm/s}$ .

Polyethylene (PE) pellets were prepared as reported elsewhere<sup>16-18</sup> with an anvil die heated on a hot plate to a temperature above the melting point of PE (136 °C); in our case the die is heated to approximately 180 °C in a fume cupboard. Approximately 0.5-1.5 mg of sample is mixed with 70 mg of PE and pressed for 2 min at 3 tons to an opaque transparent pellet in the heated die. The spectrum is collected in transmission mode. Transparent PE is an inactive material in the FIR

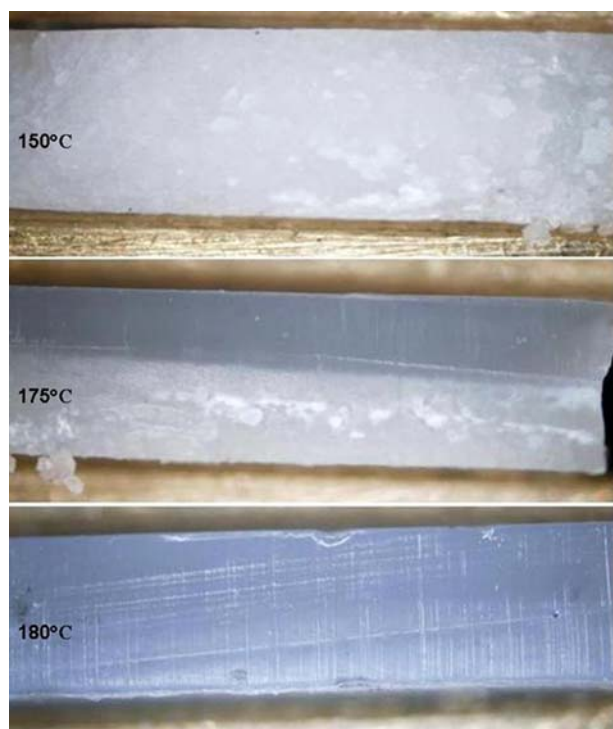


Figure 2: Photomicrographs of sectioned PE pellets produced in an anvil die heated at different temperatures: 150, 175 and 180 °C, respectively (original magnification 50x). The pellets are approximately 1 mm thick.

region and gives rise to only two small bands in the FIR spectrum. Figure 2 shows cross-sections of PE pellets pressed into shape with the heated anvil die at 150, 175 and 180 °C, respectively. At 150 °C the polyethylene is not yet melted to the desired transparent pellet; at 175 °C the pellet is becoming semitransparent (and the spectrum becomes readable although very noise filled). Only when the anvil die is heated to 180 °C on the hot plate the produced PE pellet is fully homogenous and opaque transparent.

### 3 Results and Discussion

The eight inorganic standard pigments shown here have been chosen for their different structure and absorption in the IR spectroscopic region. A pigment like Milori blue has its strongest band in the mid IR region (at 2090  $\text{cm}^{-1}$ ), whereas silicate pigments like Bavarian green earth and terra di Siena both have their strongest band around 1100-1000  $\text{cm}^{-1}$ . Lead tin yellow and cinnabar have their strongest bands below 600 and 400  $\text{cm}^{-1}$  respectively, which makes cinnabar difficult to observe in mid-IR spectroscopy. Common for these eight standard pigments is however that they all have specific and characteristic bands in the far infrared region, which makes FIR spectroscopy a viable method for their identification.

FIR Spectra of two blue pigments, Bremer and Milori blue, are shown in Figure 3. Vibrations from Bremer blue are observed for Cu-O stretching at 493 and 404  $\text{cm}^{-1}$ , Cu-OH stretching at 457 and 345  $\text{cm}^{-1}$ , O-Cu-OH bending 305 and 239  $\text{cm}^{-1}$ , out-of-plane bending modes at 197 and 173  $\text{cm}^{-1}$  and external vibrations at 251, 187, 140 and 129  $\text{cm}^{-1}$ .<sup>21-22</sup>

Milori blue has bands at 511, 496, 257 and 243  $\text{cm}^{-1}$ . The band at 511 and 496  $\text{cm}^{-1}$  is assigned to

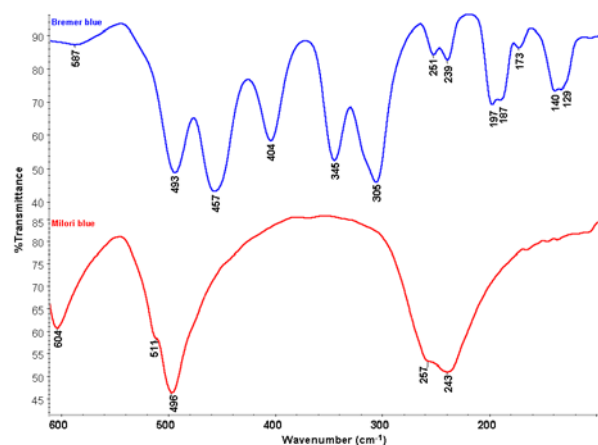


Figure 3: FIR spectra of Bremer blue (top, blue spectrum) and Milori blue (bottom, red spectrum).

Fe-CN bending and the broad band at  $243\text{ cm}^{-1}$  is assigned to C-Fe-C in-plane bending and lattice vibrations.<sup>23</sup>

FIR spectra of Viridian green and Bavarian green earth are shown in Figure 4. The FIR spectrum of Viridian green shows vibrations at 565, 552, 475 and  $410\text{ cm}^{-1}$ . Bands for Viridian are expected at 566 (br), 443 (sharp) and  $416\text{ cm}^{-1}$  according to literature.<sup>24</sup> These wavenumbers are not quite in agreement with the ones observed in our FIR spectrum. This could be due to an impurity from anhydrous chromium oxide in our standard pigment, which has bands at 555(br), 481(br) and  $420\text{ cm}^{-1}$ .<sup>24</sup> This is confirmed by Raman spectroscopy where we observe hydrated chromium oxide and anhydrous chromium oxide together with calcite as a minor impurity.

The FIR spectrum of Bavarian green earth has bands at 509, 458, 395, 371, 264 and  $228\text{ cm}^{-1}$ . This spectrum is nearly identical to the pure spectrum of quartz,<sup>25</sup> which was confirmed by the Raman spectroscopy detecting large amounts of quartz. Small amount of impurities are detected in Bavarian green earth by Raman spectroscopy coming from dolomite, calcite, hollandite and anatase as mentioned in Table 1.

Figure 5 shows the FIR spectra of two yellow pigments. Lead tin yellow vibration bands are observed at 567, 490, 449, 419, 359, 317, 289, 263, 246, 179 and  $166\text{ cm}^{-1}$ . From Raman analysis we know that there are two impurities present coming from cassiterite ( $\text{SnO}_2$ ) and massicot ( $\text{PbO}$ ). Cassiterite has strong bands at 289 and  $263\text{ cm}^{-1}$ . We observe such two bands in the spectrum of lead tin yellow, one is a shoulder band at  $294\text{ cm}^{-1}$  the other a broad band at  $263\text{ cm}^{-1}$ . A weaker band from cassiterite expected at  $510\text{ cm}^{-1}$  seems completely overlapped by the strong  $\text{PbSnO}_4$  band at  $490\text{ cm}^{-1}$ . We would expect massicot to have a broad strong band centred at  $280\text{ cm}^{-1}$  and a smaller and slimmer band at  $360\text{ cm}^{-1}$ . We observe both those bands in our lead tin yellow standard but the intensity and shape of the bands are inconsistent with those of massicot. Therefore, we have to conclude - as confirmed by Raman - that massicot is only present in very small amounts, while cassiterite is present in larger amounts; it could be detected by both, Raman as well as in the FIR spectroscopy.

Barium yellow has bands at 417, 390, 373, 336, 187, 139, 114 and  $102\text{ cm}^{-1}$ . The three bands at 417, 390 and  $373\text{ cm}^{-1}$  have been assigned to the  $\nu_4$ -vibrations of the chromate.<sup>26</sup> We observe no other impurities by Raman or FIR analysis.

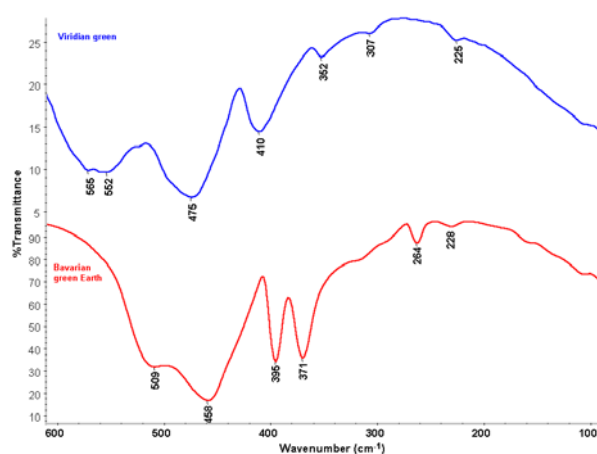


Figure 4: FIR spectra of Viridian green (top, blue spectrum) and Bavarian green earth (bottom, red spectrum).

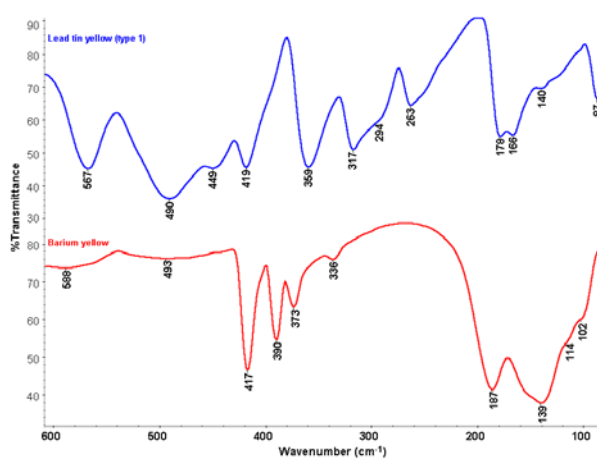


Figure 5: FIR spectra of lead tin yellow, type 1 (top, blue spectrum) and barium yellow (bottom, red spectrum).

The FIR spectrum of cinnabar is shown in Figure 6. Strong bands are observed at 345, 282 and  $126\text{ cm}^{-1}$ . These bands are in accordance with literature.<sup>27-28</sup> White, green and blue particles are detected under the microscope by Raman analysis and identified as quartz, barium white, azurite and phthalocyanine (PG36). These particle impurities are however, of very low concentration and are not strong enough to influence the FIR spectrum of cinnabar.

The vibrations for Terra di Siena are observed at 534, 454, 395, 368, 312, 262, 230, 208 and  $163\text{ cm}^{-1}$ . As in the case of Bavarian green earth we observe clearly the presence of quartz by the bands at 395 and  $368\text{ cm}^{-1}$ .<sup>25</sup> Bands at 534, 454 and  $312\text{ cm}^{-1}$  indicate clearly the presence of hematite, however this reference material has probably been grinded to much causing loss of definition of the hematite bands.<sup>29</sup> Small bands are observed below  $300\text{ cm}^{-1}$ , which originate from impurities. The presence of hematite and quartz as the major compounds is confirmed by micro-Raman analysis, where we also observe argento-

jarosite and amorphous carbon present as minor impurities.

The FIR spectra of sample AM1a and AM1b from Abbazia del Monte, together with mineral samples of calcite, quartz and hematite from Zecchi, Florence<sup>20</sup> are shown in Figure 7.

The AM1a sample, the sample showing a more bright red colour than AM1b, has bands at 540, 460, 440, 315, 227 and 103  $\text{cm}^{-1}$ . Bands at 315, 227 and 103  $\text{cm}^{-1}$  can be assigned to calcite<sup>22</sup> indicating its use as binder for the preparation of the mural paintings. The strong band of hematite expected at 304  $\text{cm}^{-1}$  and the small band at 231  $\text{cm}^{-1}$  are, unfortunately overlapped by the very strong calcite bands. However, very small bands observed in AM1a at 540, 460 and 440  $\text{cm}^{-1}$  could indicate the presence of hematite.<sup>29</sup> These two very small bands are not present in the sample

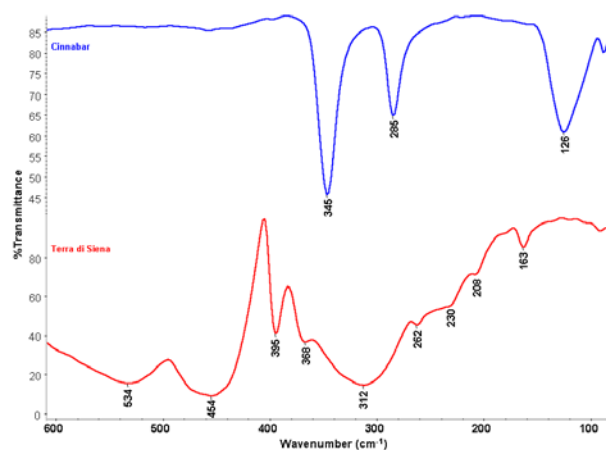


Figure 6: FIR spectra of cinnabar (top, blue spectrum) and Terra di Siena (bottom, red spectrum).

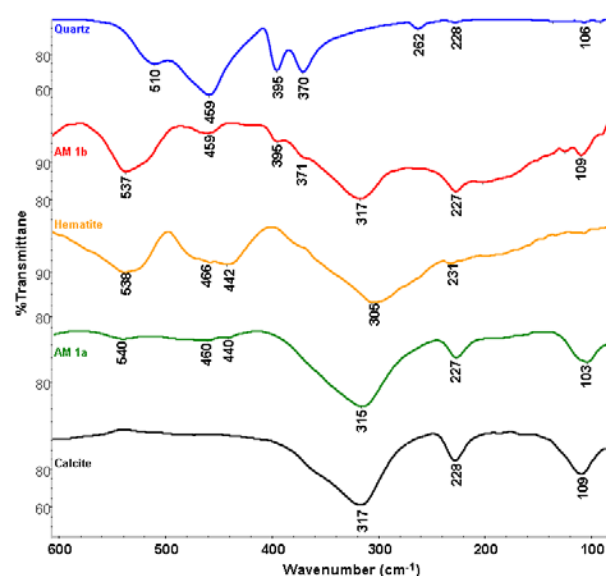


Figure 7: FIR spectra of mineral quartz (blue spectrum), sample AM1b (red spectrum), hematite (orange spectrum), sample AM1a (green spectrum) and mineral calcite (black spectrum).

AM1b (less red than AM1b). The AM1b sample shows bands at 538, 466, 395, 371, 317, 227 and 109  $\text{cm}^{-1}$ . Also here we observe strong bands coming from calcite (317, 227 and 109  $\text{cm}^{-1}$ ) and the bands at 467, 395 and 368  $\text{cm}^{-1}$  can be positively assigned to quartz.<sup>25</sup> The relatively intense band at 537  $\text{cm}^{-1}$  has yet to be identified but probably it arrives from a silicate rather than a pure quartz structure present in the AM1 sample. No hematite can be confirmed in AM1b as the band at 440  $\text{cm}^{-1}$  is missing or completely overlapped by the observed quartz band at 467  $\text{cm}^{-1}$ .

We conclude that the red AM1 sample is a complex material containing large amounts of calcite coming from the preparations of the mural paintings but it also contains small amounts of quartz and hematite, indicating a red earth or ochre pigment used for colouring the cloud beneath the Angel with a red tonality.

#### 4 Conclusion

This paper shows that FIR spectroscopy can be a useful technique for the identification of pigments. In an attempt to build up a FIR library of pigments many pigments have been recorded in transmission mode. Eight reference pigments with different IR absorptions have been presented. For all the pigments characteristic spectra in the Far-IR region have been obtained for both, mid-IR active as well as inactive compounds. Band assignment is still a difficult task and it has been possible only for compounds which have been studied in the past. It is the authors' aim to perform modelling chemical-physical studies to support the spectral interpretation.

One problem encountered during these investigations is the chemical composition of the supposed pure reference materials from the suppliers. Although they offer a realistic formula stating the main content, we observe in the FIR spectra (supported by Raman analysis) the vibrations of various impurities. In viridian green, in fact, which is supposed to be pure hydrated chromium oxide, the presence of unhydrated chromium oxide has been detected in the FIR spectrum.

Barium yellow and hematite are the only two pigments which is pure enough not to have any interfering bands coming from the impurities. These findings suggest the need to characterize carefully the supposed reference pigments prior to the establishment of reference databases and, where possible, preference should be given to pigments of mineral origin.

The red sample AM1 taken from the red cloud under the Angel in the cupola in the Abbazia del Monte was identified as a red earth pigment containing quartz and hematite. Calcite was also observed in the sample confirming its use as binder for the execution of the mural paintings.

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## 6 References

1. F. Casadio, L. Toniolo, *The analysis of polychrome works of art: 40 years of infrared spectroscopic investigations*, J. Cult. Her., 2001, **2**, 71-78.
2. R. Mazzeo, E. Joseph, S. Prati, A. Millemaggi, *Attenuated Total Reflection-Fourier transform infrared microspectroscopic mapping for the characterisation of paint cross-sections*, Anal. Chim. Acta, 2007, **599**, 107-117.
3. S. Bruni, F. Cariati, F. Casadio, L. Toniolo, *Identification of pigments on a XV century illuminated parchment by Raman and FTIR micro-spectroscopies*. Spectrochim. Acta A, 1999, **17**, 1371-1377.
4. M. Bacci, M. Picollo, *Non-destructive spectroscopic detection of cobalt(II) in paintings and glass*, Stud. Cons., 1996, **121**, 136-144.
5. A. Orlando, F. Olmi, G. Vaggelli, M. Bacci, *Mediaeval stained glasses of Pisa Cathedral (Italy): their composition and alteration products*, Analyst, 1996, **462**, 553-558.
6. R. Mazzeo, E. Joseph, *Attenuated Total Reflectance micro-spectroscopy mapping for the characterisation of bronze corrosion products*, Eur. J. Mineral., 2007, **3**, 363-371.
7. 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*, Spectrochim. Acta A, 2001, **57**, 1491-1521.
8. I.M. Bell, R.J. H. Clark, P.J. Gibbs, *Raman spectroscopic library of natural and synthetic pigments (pre- ≈ 1850 AD)*, Spectrochim. Acta A, 1997, **53**, 2159-2179.
9. I. Osticioli, A. Zoppi, E.M. Castellucci, *Fluorescence and Raman spectra on painting materials: reconstruction of spectra with mathematical methods*, J. Raman Spectr., 2006, **37**, 974-980.
10. A.V. Whitney, R.P. Van Duyne, F. Casadio, *An innovative surface-enhanced Raman spectroscopy (SERS) method for the identification of six historical red lakes and dyestuffs*, J. Raman Spectr., 2006, **37**, 993-1002.
11. L. Spinoglio, A.M. Di Giorgio, P. Saraceno, *Evolution of starbursts and AGN: Future SPICA observations*, Adv. Space Res. 2007, **40**, 684-688.
12. A.N. Salak, D.D. Khalyavin, V.M. Ferreira, J.L. Ribeiro, L.G. Vieira, *Structure refinement, far infrared spectroscopy and dielectric characterization of (1-x)La(Mg<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub>-xLa<sub>2/3</sub>TiO<sub>3</sub> solid solutions*, Appl. Phys., 2006, **99**, 094104.
13. M. Diaz, E. Huard, R. Prost, *Far infrared analysis of the structural environment of interlayer K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> selectively retained by vermiculite*, Clay. Miner., 2002, **50**, 284-293.
14. N. Vasanthan, M. Yaman, *Crystallization studies of poly(trimethylene terephthalate) using thermal analysis and far-infrared spectroscopy*, J. Polym. Sci. Pol. Phys., 2007, **45**, 1675-1982.
15. M. Mookherjee, S.A.T. Redfern, M. Zhang, *Far-infrared spectra of ammonium layer and framework silicates*, Neues Jahrb. Mineral. Monatsh., 2004, **1**, 1-9.
16. C. Karr, J.J. Kovach, *Far-infrared spectroscopy of minerals and inorganics*, Appl. Spectrosc., 1969, **23**, 219-223.
17. A. Finch, P.N. Gates, K. Radcliffe, F.N. Dickson, F.F. Bentley, *Chemical application of Far infrared spectroscopy*, Academic Press Inc., London 1970.
18. E. Kendix, G. Moscardi, R. Mazzeo, P. Baraldi, S. Prati, E. Joseph, S. Capelli, *Far infrared and Raman spectroscopy analysis of inorganic pigments*, J. Raman Spectrosc. 2008, **39**, 1104-1112.
19. Kremer Pigmente homepage, <http://kremer-pigmente.de/> (accessed 12/09/2007).
20. Homepage of Zecchi in Florence, <http://www.zecchi.it/> (accessed 12/03/2008).
21. R.L. Frost, W.N. Martens, L. Rintoul, E. Mahmutagic, J.T. Kloppogge, *Raman spectroscopic study of azurite and malachite at 298 and 77 K*, J. Raman Spectr., 2002, **33**, 252-259.
22. W.B. White, *The carbonate minerals*, in: V. C. Farmer (ed.), *The infrared spectra of mineral*, Mineralogical Society Monograph 4, The Mineralogical Society, London 1974, 227-284.
23. S.N. Ghosh, *Infrared spectra of the Prussian blue analogues*, J. Inorg. Nucl. Chem., 1974, **36**, 2465-2466.
24. R. Newman, *Some applications of infrared spectroscopy in the examination of painting materials*, J. Am. Inst. Conserv., 1974, **19**, 42-62.
25. H.H. Moenke, *Silica, the three-dimensional silicate, borosilicates and beryllium silicates*, in: V.C. Farmer (ed.), *The infrared spectra of mineral*, Mineralogical Society Monograph 4, The Mineralogical Society, London 1974, 365-444.
26. S.D. Ross, *Sulphates and other oxy-anions of group VI*, in: V.C. Farmer (ed.), *The infrared spectra of mineral*, Mineralogical Society Monograph 4, The Mineralogical Society, London, 1974, 423-444.
27. U.B. Mioč, Ph. Colomban, G. Sagon, M. Stojanović, A. Rosič, *Ochre decor and cinnabar residues in Neolithic pottery from Vinča, Serbia*, J. Raman Spectr., 2004, **34**, 843-846.
28. H.H.W. Moenke, *Vibrational spectra and the crystal-chemical classification of minerals*, in: V. C. Farmer (Ed.), *The infrared spectra of mineral*, Mineralogical Society Monograph 4, The Mineralogical Society, London, 1974, 111-118.
29. J.L. Rendon, C.J. Serna, *IR Spectra of powder hematite: effects of particles size and shape*, Clay Miner., 1981, **16**, 375-381.