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⁻¹) 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,¹ ² parchment,³ glass⁴ ⁵ and corrosion products.⁶ 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 limitations⁷ ⁸ 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 mathematical⁹ or instrumental methods.¹⁰

FIR spectroscopy is used in different fields such as astrophysical,¹¹ cation exchange and interactions in ceramics¹² ¹³ and lattice vibrations in the field of polymer crystallisation.¹⁴ Recent studies reported the use of FIR spectroscopy to distinguish between different micas.¹⁵ Studies from 1969 highlight its analytical potential for the investigation of minerals in the 200-50 cm⁻¹ region,¹⁶ other studies discuss the assignment of external vibrations in liquid and solid phases.¹⁷ However, only a few articles about FIR spectroscopy applied in the field of cultural heritage have been published¹⁶ ¹⁸ and for this reason
the creation of a FIR library of artistic and corrosion materials is of outmost 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. One standard pigment, hematite (Fe₂O₃) was purchased from Zecchi in Florence. 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).

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Provenance</th>
<th>Chemical composition*</th>
<th>Raman identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bremer blue</td>
<td>Kremer pigment 10180</td>
<td>2CuCO₃·Cu(OH)₂</td>
<td>2CuCO₃·Cu(OH)₂ + Quartz (SiO₂)</td>
</tr>
<tr>
<td>Milori blue</td>
<td>Kremer pigment 45200</td>
<td>FeN₄Fe(CN)₆</td>
<td>Fe₄[Fe(CN)₆]₁₄·16H₂O + small impurities Cuprite (Cu₂O) and Hausmannite (Mn₃O₄)</td>
</tr>
<tr>
<td>Viridian green</td>
<td>Kremer pigment 44250</td>
<td>Cr₂O₃·2H₂O</td>
<td>Cr₂O₃·2H₂O + Cr₂O₃ + small impurity Calcite (CaCO₃)</td>
</tr>
<tr>
<td>Bavarian green</td>
<td>Kremer pigment 11100</td>
<td>Al, K, Mg, Ca, Fe-silicates</td>
<td>Quartz (SiO₂) + small amount of impurities: Hollandite (BaMn(II)Mn(IV)O₁₈) + Anatase (TiO₂) + Calcite (CaCO₃) + Dolomite (CaMg(CO₃)₂)</td>
</tr>
<tr>
<td>Lead tin yellow</td>
<td>Kremer pigment 10110</td>
<td>Pb₂SnO₄</td>
<td>Lead tin yellow (Pb₂SnO₄) + cassiterite (SnO₂) + massicot (PbO)</td>
</tr>
<tr>
<td>Barium yellow</td>
<td>Kremer pigment 43940</td>
<td>BaCrO₄</td>
<td>Barium yellow (BaCrO₄)</td>
</tr>
<tr>
<td>Cinnabar</td>
<td>Kremer pigment 10625</td>
<td>HgS</td>
<td>HgS + particle impurities: Quartz (SiO₂) + Barium white (BaSO₄) + Azurite (2CuCO₃·Cu(OH)₂) + Phthalocyanine PG36 (C₃₂Br₆Cl₁₀CuN₈)</td>
</tr>
<tr>
<td>Terra di Siena (burnt)</td>
<td>Kremer pigment 40450</td>
<td>Hematite (Fe₂O₃), amorphous silica with impurities (1-10%) MnO₂, alumina, CaCO₃</td>
<td>Hematite (Fe₂O₃) + Quartz (SiO₂) + Argentojarosite (AgFe₂(SO₄)₃(OH)₂) + C (amorphous)</td>
</tr>
<tr>
<td>Hematite</td>
<td>Zecchi, Florence</td>
<td>Fe₂O₃</td>
<td>Hematite (Fe₂O₃)+ C (amorphous)</td>
</tr>
<tr>
<td>Quartz</td>
<td>Geological Museum, University of Bologna, Italy</td>
<td>SiO₂</td>
<td>No Raman, but powder XRD analysis confirms that the sample is pure. The mineral sample originates from Reggio Emilia, Italy.</td>
</tr>
<tr>
<td>Calcite</td>
<td>Geological Museum, University of Bologna, Italy</td>
<td>CaCO₃</td>
<td>No Raman, but powder XRD analysis confirms that the sample is pure. The mineral sample originates from Posso Raticosa, Bolivia.</td>
</tr>
</tbody>
</table>

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.

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 where taken during recent restoration work of Abbazia del Monte in Cesena, Italy.
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 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 cm\(^{-1}\) and a mirror velocity of 0.6329 cm/s.

Polyethylene (PE) pellets were prepared as reported elsewhere\(^{16-18}\) 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 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 cm\(^{-1}\)), whereas silicate pigments like Bavarian green earth and terra di Siena both have their strongest band around 1100-1000 cm\(^{-1}\). Lead tin yellow and cinnabar have their strongest bands below 600 and 400 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 cm\(^{-1}\), Cu-OH stretching at 457 and 345 cm\(^{-1}\), O-Cu-OH bending 305 and 239 cm\(^{-1}\), out-of-plane bending modes at 197 and 173 cm\(^{-1}\) and external vibrations at 251, 187, 140 and 129 cm\(^{-1}\).\(^{21-22}\)

Milori blue has bands at 511, 496, 257 and 243 cm\(^{-1}\). The band at 511 and 496 cm\(^{-1}\) is assigned to...
Fe-CN bending and the broad band at 243 cm$^{-1}$ is assigned to C-Fe-C in-plane bending and lattice vibrations.$^{23}$

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 cm$^{-1}$. Bands for Viridian are expected at 566 (br), 443 (sharp) and 416 (sharp) cm$^{-1}$ according to literature.$^{24}$ 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(w) cm$^{-1}$. 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 cm$^{-1}$. This spectrum is nearly identical to the pure spectrum of quartz,$^{25}$ 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 cm$^{-1}$. From Raman analysis we know that there are two impurities present coming from cassiterite ($\text{SnO}_2$) and massicot (PbO). Cassiterite has strong bands at 289 and 263 cm$^{-1}$. We observe such two bands in the spectrum of lead tin yellow, one is a shoulder band at 294 cm$^{-1}$ the other a broad band at 263 cm$^{-1}$. A weaker band from cassiterite expected at 510 cm$^{-1}$ seems completely overlapped by the strong PbSnO$_4$ band at 490 cm$^{-1}$. We would expect massicot to have a broad strong band centred at 280 cm$^{-1}$ and a smaller and slimmer band at 360 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 cm$^{-1}$. The three bands at 417, 390 and 373 cm$^{-1}$ have been assigned to the $\nu_4$-vibrations of the chromate.$^{26}$ We observe no other impurities by Raman or FIR analysis.

The FIR spectrum of cinnabar is shown in Figure 6. Strong bands are observed at 345, 282 and 126 cm$^{-1}$. These bands are in accordance with literature.$^{27,28}$ 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 cm$^{-1}$. As in the case of Bavarian green earth we observe clearly the presence of quartz by the bands at 395 and 368 cm$^{-1}$. Bands at 534, 454 and 312 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.$^{29}$ Small bands are observed below 300 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 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 cm\(^{-1}\). Bands at 315, 227 and 103 cm\(^{-1}\) can be assigned to calcite indicating its use as binder for the preparation of the mural paintings. The strong band of hematite expected at 304 cm\(^{-1}\) and the small band at 231 cm\(^{-1}\) are, unfortunately overlapped by the very strong calcite bands. However, very small bands observed in AM1a at 540, 460 and 440 cm\(^{-1}\) could indicate the presence of hematite. These two very small bands are not present in the sample AM1b (less red than AM1b). The AM1b sample shows bands at 538, 466, 395, 371, 317, 227 and 109 cm\(^{-1}\). Also here we observe strong bands coming from calcite (317, 227 and 109 cm\(^{-1}\)) and the bands at 467, 395 and 368 cm\(^{-1}\) can be positively assigned to quartz. The relatively intense band at 537 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 cm\(^{-1}\) is missing or completely overlapped by the observed quartz band at 467 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 assignation 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