Volume 1 | Number 1 | Jan 2013 | Pages 1–100

# Analytical Methods

www.rsc.org/methods

ROYAL SOCIETY OF CHEMISTRY

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

www.rsc.org/methods

# Journal Name

## ARTICLE

# Portable Diffuse Reflectance Infrared Fourier Transform (DRIFT) Technique for the Non-invasive Identification of Canvas Ground: IR Spectra Reference Collection

M. Manfredi*[a,c], E. Barberis[c], A. Rava[b], E. Robotti[a], F. Gosetti[a] and E. Marengo[a]

The method for preparing paintings varies from artist to artist. The non-destructive investigation of the preparation used to make a canvas is very important both for restoration and authentication purposes. A portable diffuse reflectance infrared Fourier transform (DRIFT) method for the non-invasive characterization of grounds in paintings is presented: with this method there is no need to sample or touch the artworks and the analysis can be performed directly on site. Sixteen of the most important canvas grounds used since the XIV to the XX century were prepared following the ancient recipes: they include grounds from Vasari, Caravaggio, and De Chirico. The grounds were analyzed with DRIFT spectroscopy and a reference spectra collection was built. The DRIFT method was then performed on the ground of a Moncalvo's painting: the infrared analysis was able to identify the ground composition. Portable DRIFT method can be applied as non-invasive diagnostic tool in cultural heritage field: useful information can be provided to conservators and art historians.

## Introduction

Paintings are made by different layers of material, which roughly are support, primer, different layers of paint and varnish. Other layers such as glue, a preparatory drawing, an imprimatur and additional layers of paint can complement the painting structure. Moreover, the material composition of paintings is often dominated by composite materials constituted by different chemical substances.

Canvas ground is the layer or group of layers that are between the canvas support and the painting surface (Fig. 1). For both technical and aesthetical reasons ground is made by a thin layer of inert material mixed with binder and often colored with pigments: applied on a canvas support it is used to reduce the color absorption and to protect the fibers constituting the painting support from degradation.



Fig. 1: Layers which make up the structure of a painting.

Since the antiquity, artists used grounds to keep the canvas surface more uniform, flat and to reduce weave irregularities. There are several kinds of grounds. Knowing the type of ground that was used is very important for conservative purposes: for example the binders used can affect the degradation of the paint film. In particular, if the composition of ground and color binder is not the same, the degradation may accelerate and the restoration may results challenging. Moreover, grounds, like pictorial techniques, are often the digital fingerprint of artists and historical periods and they can be used to validate the painting authenticity.

In recent years, several analytical methods have been employed for the investigation and characterization of cultural heritage objects. Analytical methodologies that require micro sampling or no sampling are always preferred.

FTIR spectroscopy has long been used for the analysis and characterization of objects of art in support of the efforts to preserve and restore them. The stratigraphic information, useful to art historians and restorers, can be obtained by studying cross sections with optical and electronic microscopy, micro-FTIR and Raman spectroscopy. Typical applications include analysis of paint pigments and binders, lacquers and finishes[1]. FTIR has been used also to measure and monitor the deterioration of artworks and to support conservators[2, 3].

A series of paint cross sections from an oil painting were studied by attenuated total reflection in conjunction with Fourier transform infrared spectroscopy (ATR-FTIR)[4-7] .

A recent study demonstrated the possibilities offered by macro-ATR-FT-IR imaging for a simple identification of the different compounds present in paint cross-sections [8].

A statistic approach using principal component analysis for the interpretation of the hyperspectral data arrays obtained by μATR-FTIR of paint cross-sections was proposed[9].

Unfortunately most of FTIR spectrometers are located in labs, therefore the measurement often requires to work on a small sample taken from the artwork. Moreover, often, a micro sampling may not be representative of the area that must be analyzed and then an accurate assessment of the artwork is not possible because it would require too many samples of the artifact. On particularly precious paintings sampling is usually forbidden: this suggests the need of an in situ non-invasive techniques for the analysis.

Several in-situ techniques have been employed for the non-invasive investigation of objects of art. In particular mid-infrared reflectance spectroscopy has been used to study modern art materials and metal-oxalate complexes on polychrome artwork surfaces [10-14]. The diffuse reflectance spectra are very similar to those obtained from transmission mode but overtones and combination bands increase their signals because of many reflections take place. The interpretation of the vibrational profiles is often difficult because of the appearing of distortions with respect to the spectra acquired in the conventional acquisition mode: some distortions appear as derivative-like spectral features and inverted bands, following the Reststrahlen effect. The distortion arising from the volume and surface reflection can be corrected by using Kubelka-Munk (KM) and Kramers-Kronig (KK) correction, but in case of complex morphology and heterogeneity of the surface, like for real artworks, their use is limited[15, 16].

The applicability of a diffuse reflectance infrared Fourier transform handled device to perform in situ analysis on cultural heritage has already been discussed: in situ measurements were compared with the laboratory measurements in order to validate the information obtained from the handled instrument. The authors shown that using the handled device the specular reflectance contribution is lower than using a more classic Fiber Optic Reflectance Spectroscopy which has a normal optical layout (0°/0° geometry) in which the collection of the specular reflected light is favoured.[17]. Therefore, correction algorithms (KK and KM) couldn't be applied to the reflectance infrared data obtained from their handled device.

In this work we report a portable diffuse reflectance infrared Fourier transform (DRIFT) method for the non-invasive characterization of grounds in painting: with this method there is no need to touch the sample and the analysis can be done directly on site.

No sample needs to be taken to analyze the object, and in fact, also a large number of areas can be analyzed quickly and in a non-destructive manner.

The main purpose of this research is to demonstrate the potentiality of the technique and to provide a reference library of DRIFT infrared spectra of the most used canvas grounds.

16 canvas grounds were prepared following the recipes and procedures of the most important artists from XIV to XX century like Vasari, Mantegna, Veronese, Caravaggio and De Chirico and analyzed using DRIFT. The portable DRIFT and the reference library were then used to identify the ground used by the Moncalvo, who can be considered one of the most important artists of Piedmont (Italy) in the XVI century, on its

painting "Madonna con bambino tra San Rocco e San Michele", that was confirmed by the historians.

## Experimental

### Canvas ground preparation

Canvas ground is the layer or group of layers that are between the canvas support and the paint layer. Since medieval, canvas has been used for painting: from the XV century, with the spreading of tempera paint, canvases were prepared using rabbit skin glue. Successively, artists introduced the use of fine gypsum. In the XVI century, the use of oil paints brought painters to mix pigments and colours in ground mixture. Then, the addition of flour, oil and white lead was introduced in the preparation receipts. During the XVII and the XVIII centuries painters used clays, while in the XIX century they employed white zinc. In the last century new receipts were experimented introducing white titanium (titanium oxide) and synthetic resins.

Table 1 shows the 16 grounds prepared and analysed by DRIFT spectroscopy.

| Samples | Receipts |
|---------|----------|
| Ground 1 [18] (XV century) | rabbit skin glue |
| Ground 2 [18] (Bellini, Mantegna, Tiziano) | gypsum, rabbit skin glue and honey |
| Ground 3 [19] (Vasari) | lower layer: flour, linseed oil, white lead, rabbit skin glue; upper layer: yellow lead (PbO), black vine, stand oil, white lead $((PbCO_3)_2 \cdot Pb(OH)_2)$ |
| Ground 4 [19] (Vasari) | lower layer: flour, linseed oil, white lead $((PbCO_3)_2 \cdot Pb(OH)_2)$, rabbit skin glue; upper layer: red lead $(Pb_3O_4)$, black vine, stand oil |
| Ground 5 [20] (Armenini – XVI) | flour, walnut oil and white lead $((PbCO_3)_2 \cdot Pb(OH)_2)$ |
| Ground 6 [18] (Caliari-Veronese) | gypsum and rabbit skin glue (lower layer); linseed oil, white lead, red ochre $(Fe_2O_3)$ and yellow earth $(Fe_2O_3)$ (upper layer) |
| Ground 7 [21] (Caravaggio) | red bole $(Fe_2O_3$ (red hematite) and silicate), yellow earth $(FeO(OH))$, stand oil, white lead $((PbCO_3)_2 \cdot Pb(OH)_2)$, black vine, sand and cinnabar $(HgS)$ |
| Ground 8 [22] (Van Baburen, caravaggesque) | red bole $(Fe_2O_3$ (red hematite) and silicate), stand oil, Venetian turpentine (pine resin), egg and sand |
| Ground 9 [23] (Volpato) | red bole $(Fe_2O_3$ (red hematite) and silicate), stand oil, Siena earth $(Fe_2O_3)$ and raw umber $(Fe_2O_3$ and $MnO_2)$ |
| Ground 10 [24] (De Mayerne) | litargirium oil (stand oil + yellow lead), red lead $(Pb_3O_4)$, yellow earth $(FeO(OH))$ and black vine |
| Ground 11 [24] (De Mayerne) | litargirium oil (stand oil + yellow lead) and yellow earth $(FeO(OH))$ |

| Ground 12 [18] (Jan Vermeer) | kaolin, white lead, yellow earth (FeO(OH)), rabbit skin glue, stand oil |
|---|---|
| Ground 13 [25] (Max Doerner) | gypsum, zinc white, rabbit skin and stand oil |
| Ground 14 [26] (Pierre A. Renoir) | white lead, kaolin, stand oil |
| Ground 15 [27] (De Chirico) | Meudon white, egg yolk, poppy oil, Venetian turpentine, white vinegar, glycerin, water |
| Ground 16 [18] (recent synthetic binders) | titanium white, chalk, acrylic resin and kaolin |

Table 1: description of the 16 grounds, from XIV to XX century receipts, prepared and analysed by DRIFT spectroscopy.

**DRIFT analysis**

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) was performed with an Agilent 4100 Exoscan FTIR portable spectrometer (Agilent Technologies, Santa Clara, CA, USA) with a diffuse reflectance sampling interface.

Sample spectra were obtained in absorption mode using a diffuse reflectance device over a wavelength interval from 650 cm-1 to 4000 cm-1 at 32 scans per sample and a resolution of 4 cm-1. The system has a ZnSe beam splitter and a DTGS detector. The background was acquired with a diffuse gold reference cap and the spectra treatments were performed using a OPUS 5.5 software (Bruker, Billerica, MA, USA). In this handled device the optical head measures a higher proportion of the diffuse reflectance signal and a low proportion of the specular one that gives a less distorted spectrum.

The spot size of the beam was estimated about 2 mm and the time required to perform a full scan was about 15 seconds. The measurements were performed holding the instrument by hand and using a support in order to keep the DRIFT stable and close to the samples. Three DRIFT spectra of each sample were collected in different position and the average spectra was used for identification purposes.

**Results and discussions**

The 16 grounds prepared following the original receipts of the most relevant painters of the world from the XV to XX centuries were analysed by using a portable DRIFT spectrometer. The analysis was carried out just pointing the infrared beam on the ground surface without touching the sample. The surface reflection gives several types of distortions due to derivative shape, Reststrahlen effect, and intensity enhancement. When the area affected by the Reststrahlen effect did not overlap the signal of other compounds the identification of the collected information was performed also on the range of the spectra below 1400 cm-1. The identification has been based on the raw spectra without using the corrections algorithms K-K and K-M.

Ground 1 (XV century): rabbit skin glue.

The sample ground 1 was prepared spreading rabbit skin glue on the canvas. Figure 2 shows the IR spectra of the sample ground 1, in particular of the rabbit skin glue: the strong and broad band centred near 3500 cm-1 is assigned to the stretching of NH groups, near 2900 cm-1 there are the C-H stretching

bands. The peak at 1690 cm-1 is of the C=O stretching band and at 1574 cm-1 there is the bending band of the C-N-H. Peak at 1464 cm-1 represents the bending band of C-H [7].
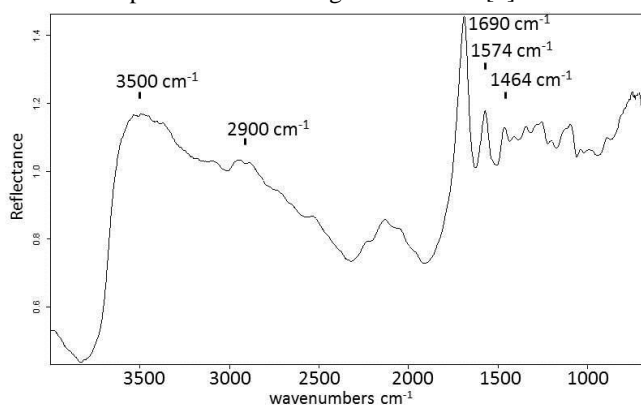


Fig. 2: DRIFT infrared spectra of ground 1 prepared with rabbit skin glue.

Ground 2 (Bellini, Mantegna, Tiziano): Gypsum, rabbit skin glue and honey.

Figure 3 shows the IR spectra of sample ground 2: the strong and broad band between 3700 and 3200 cm-1 is assigned to the anti-symmetric and symmetric O-H stretching bands of gypsum[7]. The peaks at 1679 and 1632 cm-1 are the deformation vibrations of the O-H bond of water[28]. Due to the high adsorption index k the asymmetric $SO_4^{2-}$ stretching band of gypsum is affected by the Reststrahlen effect and consequently appears as inverted band showing the minima at about 1152 cm-1. The enhancement of second-order and combination bands, due to diffuse reflection, is evident in the range 2500-1900 cm-1. In the reflection spectrum of gypsum both the modes $v_1 + v_3$ and $2v_3$ are covered by a strong and broad band at 2220 cm-1 due to the combination of bending and vibration modes of $H_2O$ [10] .Near 2900 cm-1 there are the C-H stretching bands of the rabbit skin glue. The signal at 1258 cm-1 is assigned to the honey [10].
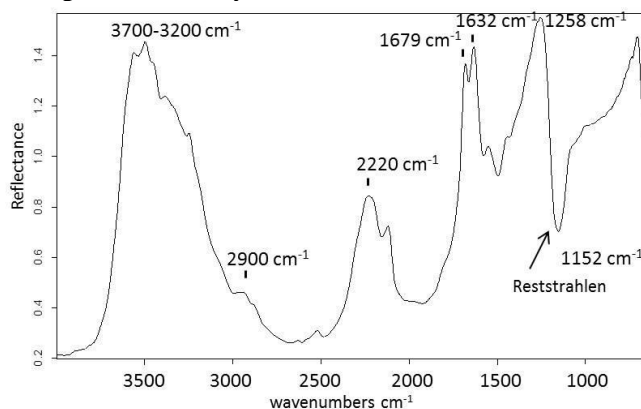


Fig. 3: DRIFT infrared spectra of ground 2 prepared with gypsum, rabbit skin glue and honey.

Ground 3 (Vasari): lower layer: flour, linseed oil, white lead, rabbit skin glue; upper layer: yellow lead (PbO), black vine, stand oil, white lead ($(PbCO_3)_2 \cdot Pb(OH)_2$).

In figure 4 it is represented the IR spectrum of the sample ground 3: the priming layer is comprised of lead white, identified by the distorted $v_3$ Reststrahlen band of $CO_3^{2-}$ at 1392 cm-1 and by the peak at 3539 cm-1 due to the $Pb(OH)_2$ moiety.

The typical shape of combination band of $\nu_1 + \nu_3$ at about 2400 $cm^{-1}$ is due to the $((PbCO_3)_2 \cdot Pb(OH)_2)$ structure [10]. Stand oil could be clearly identified by the C-H stretching bands at 2945 and 2865 $cm^{-1}$, by the stretching band of the C=O at 1750 $cm^{-1}$, by the C-H bending at 1481 $cm^{-1}$ and by the signal at 1177 $cm^{-1}$. The small peaks at 1708 $cm^{-1}$ and at 1576 $cm^{-1}$ are respectively of the C=O stretching and of the C-N-H bending of the rabbit skin glue[7].
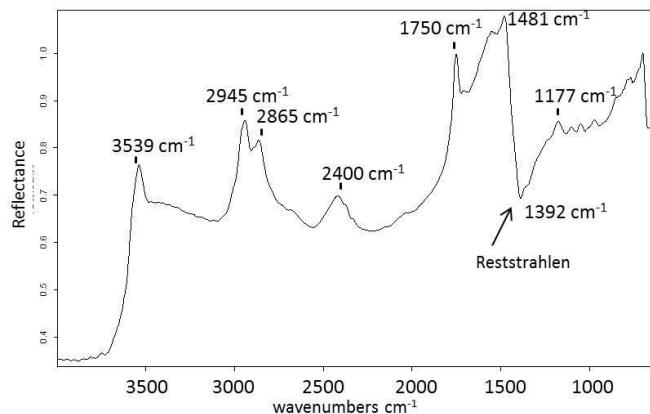


Fig. 4: DRIFT infrared spectra of ground 3 prepared with flour, linseed oil, white lead, rabbit skin glue (lower layer) and yellow lead (PbO), black vine, stand oil, white lead $((PbCO_3)_2 \cdot Pb(OH)_2)$ (upper layer).

Ground 4 (Vasari): lower layer: flour, linseed oil, white lead$((PbCO_3)_2 \cdot Pb(OH)_2)$, rabbit skin glue; upper layer: red lead $(Pb_3O_4)$, black vine, stand oil.
Figure 5 shows the IR spectra of sample ground 4. The infrared spectra is similar to the one of sample ground 3: the presence of lead white is identified by the peak at 3539 $cm^{-1}$ due to $Pb(OH)_2$ moiety and by the combination band of $\nu_1 + \nu_3$ at about 2400 $cm^{-1}$ due to the $((PbCO_3)_2 \cdot Pb(OH)_2)$ structure [10]. Stand oil could be identified by the C-H stretching band at 2945 and 2865 $cm^{-1}$, by the stretching band of the C=O at 1750 $cm^{-1}$, by the C-H bending at 1481 $cm^{-1}$ and by the signal at 1177 $cm^{-1}$. The small peak at 1709 $cm^{-1}$ and the one at 1574 $cm^{-1}$ are respectively of the C=O stretching and of the C-N-H bending of the rabbit skin glue[7].
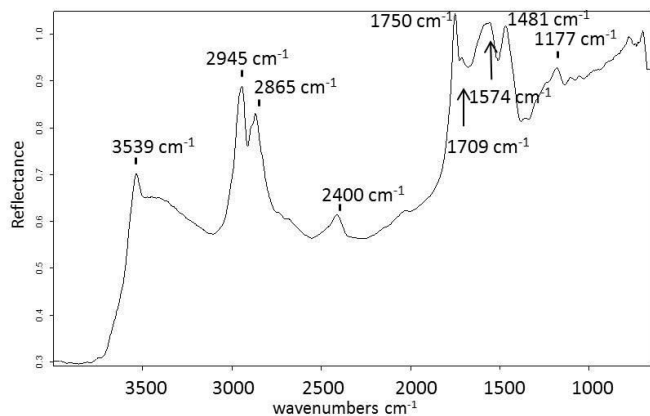


Fig. 5: DRIFT infrared spectra of ground 4 prepared with flour, linseed oil, white lead $((PbCO_3)_2 \cdot Pb(OH)_2)$, rabbit skin glue (lower layer) and red lead $(Pb_3O_4)$, black vine, stand oil (upper layer).

Ground 5 (Armenini – XVI): flour, walnut oil and white lead $((PbCO_3)_2 \cdot Pb(OH)_2)$.
In figure 6 it is presented the IR spectra of sample ground 5: the quality of the spectra is poor but lead white can be identified by the distorted $\nu_3$ Reststrahlen band of $CO_3^{2-}$ at 1396 $cm^{-1}$, by the small peak at 3539 $cm^{-1}$ due to the $Pb(OH)_2$ moiety and by the typical band at about 2400 $cm^{-1}$ due to the $((PbCO_3)_2 \cdot Pb(OH)_2)$ structure [10]. The peaks at 2945 and 2868 $cm^{-1}$ are the C-H stretching bands of the walnut oil. At 1750 $cm^{-1}$ there is the stretching band of the C=O, the C-H bending is visible at 1497 $cm^{-1}$[7].
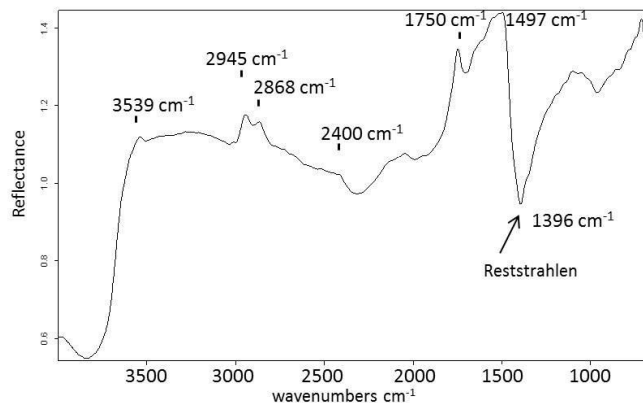


Fig. 6: DRIFT infrared spectra of ground 5 prepared with flour, walnut oil and white lead $((PbCO_3)_2 \cdot Pb(OH)_2)$.

Ground 6 (Caliari-Veronese): gypsum and rabbit skin glue (lower layer); linseed oil, lead white, red ochre $(Fe_2O_3)$ and yellow earth $(FeO(OH))$ (upper layer).
In figure 7 it is presented the IR spectra of sample ground 6: lead white can be identified by the distorted $\nu_3$ Reststrahlen band of $CO_3^{2-}$ at 1396 $cm^{-1}$, by the peak at 3539 $cm^{-1}$ due to the $Pb(OH)_2$ moiety and by the typical band at about 2400 $cm^{-1}$ due to the $((PbCO_3)_2 \cdot Pb(OH)_2)$ structure [10]. Linseed oil could be identified by the peaks at 2925 and 2857 $cm^{-1}$ of the C-H stretching bands, at 1742 $cm^{-1}$ of the stretching band of the C=O and the C-H bending at 1497 $cm^{-1}$[7].. The band at 1060 $cm^{-1}$ has been included as a tentative indication of a possible presence of silicate compounds of ochre (yellow earth)[12].
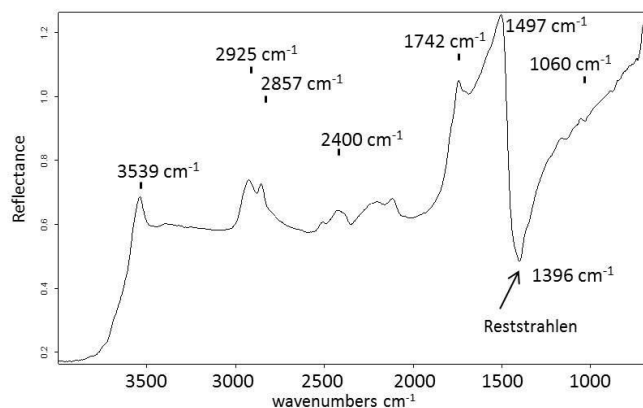


Fig. 7: DRIFT infrared spectra of ground 6 prepared with gypsum and rabbit skin glue (lower layer) and linseed oil, white lead, red ochre $(Fe_2O_3)$ and yellow earth $FeO(OH)$ (upper layer).

Ground 7 (Caravaggio): red bole ($Fe_2O_3$ (red hematite) and silicate), yellow earth FeO(OH), stand oil, white lead (($PbCO_3)_2 \cdot Pb(OH)_2$), black vine, sand and cinnabar (HgS).

In figure 8 it is represented the IR spectra of sample G7: stand oil is described the peaks at 2946 and 2868 $cm^{-1}$ of the C-H stretching bands, at 1740 $cm^{-1}$ of the stretching band of the C=O, by the C-H bending at 1463 $cm^{-1}$. White lead can be identified by the peak at 3539 $cm^{-1}$ due to the $Pb(OH)_2$ moiety and by the band at about 2400 $cm^{-1}$ due to the (($PbCO_3)_2 \cdot Pb(OH)_2$) structure [10]. The primary inorganic material in the red bole is a clay: there are silicate bands near 3600 $cm^{-1}$. The strong band at 1080 $cm^{-1}$ is assigned to the Si-O asymettric stretching mode as a tentative indication of the presence of silicate component (quartz) of red ochre which is the main component of red bole[31].
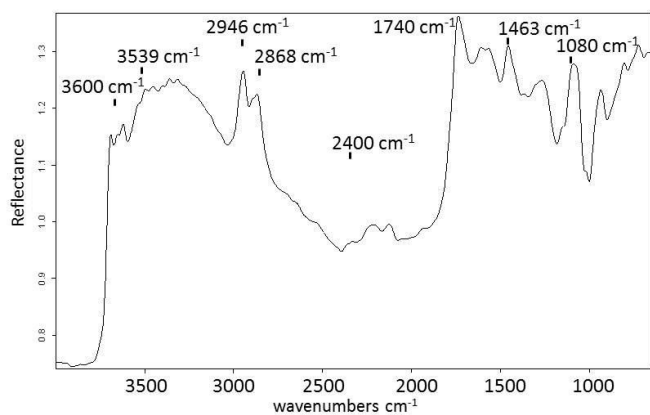


Fig. 8: DRIFT infrared spectra of ground 7 prepared with red bole ($Fe_2O_3$ (red hematite) and silicate), yellow earth FeO(OH), stand oil, white lead (($PbCO_3)_2 \cdot Pb(OH)_2$), black vine, sand and cinnabar (HgS).

Ground 8 (Van Baburen, caravaggesque): red bole ($Fe_2O_3$ (red hematite)and silicate), stand oil, Venetian turpentine (pine resin), egg and sand.

In figure 9 it is represented the IR spectra of sample ground 8: stand oil is described by the two stretching bands of $CH_2$ at 2958 and 2877 $cm^{-1}$, by the stretching band of the C=O at 1756 $cm^{-1}$ and by the C-H bending at 1463 $cm^{-1}$. There are silicate bands near 3600 $cm^{-1}$ of red bole and sand. Peak at 1395(C-C stretching bands), 1270 $cm^{-1}$,1125 $cm^{-1}$ and 1070 $cm^{-1}$ are assigned to the Venetian turpentine[7]. The presence of egg (proteinaceus binder) is identified by the signals at 1660 $cm^{-1}$ (amide I) and 3309 $cm^{-1}$ (NH)[10].
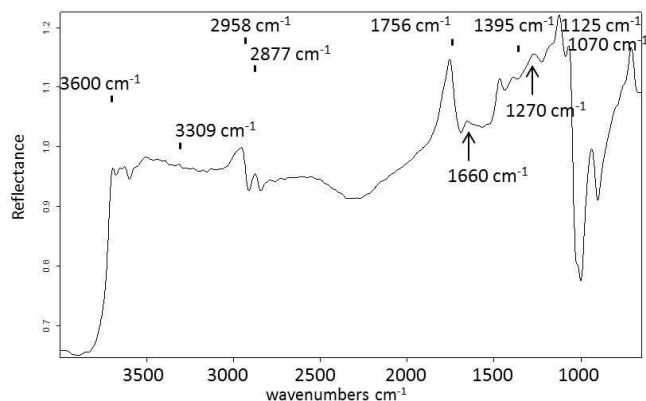


Fig. 9: DRIFT infrared spectra of ground 8 prepared with red bole ($Fe_2O_3$ (red hematite)and silicate), stand oil, Venetian turpentine (pine resin), egg and sand.

Ground 9 (Volpato): red bole ($Fe_2O_3$ (red hematite)and silicate), stand oil, Siena earth ($Fe_2O_3$) and raw umber ($Fe_2O_3$ and $MnO_2$).

Figure 10 shows the IR spectra of sample ground 9: the two bands at 2950 and 2872 $cm^{-1}$ are the $CH_2$ stretching bands of the stand oil, and the peak at 1752 $cm^{-1}$ is its stretching band of C=O. There are silicate bands near 3600 $cm^{-1}$ of red bole. At 1112 $cm^{-1}$ and 1070 $cm^{-1}$ there are the peaks assigned to Siena earth and raw umber respectively[30].
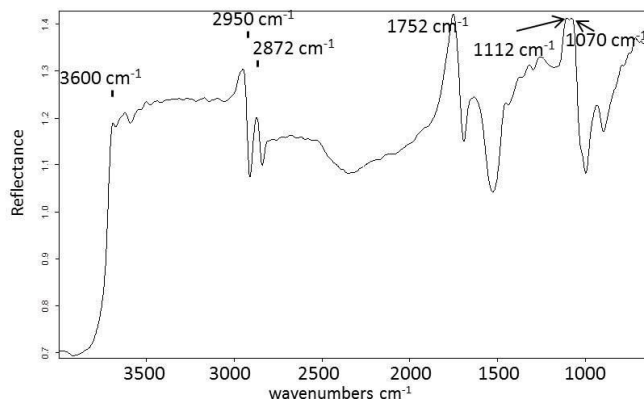


Fig. 10: DRIFT infrared spectra of ground 9 prepared with red bole ($Fe_2O_3$ (red hematite)and silicate), stand oil, Siena earth ($Fe_2O_3$) and raw umber ($Fe_2O_3$ and $MnO_2$).

Ground 10 (De Mayerne): litargirium oil (stand oil + yellow lead), red lead ($Pb_3O_4$), yellow earth FeO(OH)and black vine.

Figure 11 shows the IR spectra of sample ground 10: the two bands at 2944 and 2865 $cm^{-1}$ are the $CH_2$ stretching bands of the stand oil and the peak at 1738 $cm^{-1}$ is its stretching band of the C=O.

The absence of silicates signals in the infrared spectra of ground 10 can be explained by the low amount of earth materials used to prepare the ground.
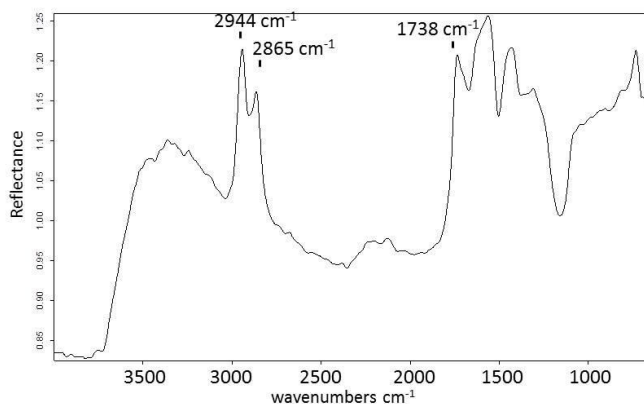


Fig. 11: DRIFT infrared spectra of ground 10 prepared with litargirium oil (stand oil + yellow lead), red lead ($Pb_3O_4$), yellow earth FeO(OH) and black vine.

Ground 11 (De Mayerne): litargirium oil (stand oil + yellow lead) and yellow earth FeO(OH).

Figure 12 shows the IR spectra of sample ground 11: the two bands at 2947 and 2870 cm$^{-1}$ are the CH$_2$ stretching bands of the stand oil and the peak at 1739 cm$^{-1}$ is its stretching band of C=O. The peak at 1374 cm$^{-1}$ is assigned at the bending vibrations of the CH$_3$[30]. The absorption band at about 3400 cm$^{-1}$ is assigned at the alcohol and/or hydro-peroxide vibrations both products of oil oxidation.
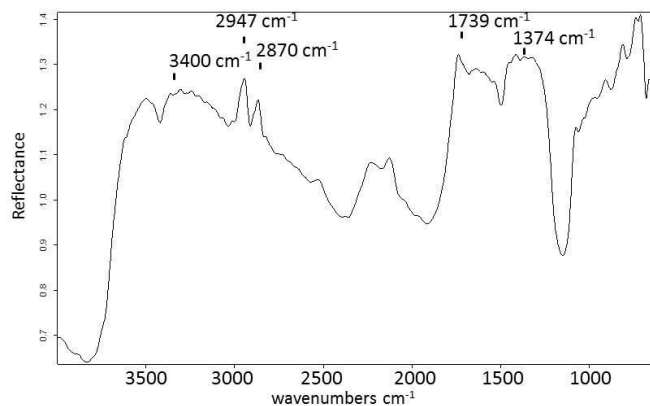


Fig. 12: DRIFT infrared spectra of ground 11 prepared with litargirium oil (stand oil + yellow lead) and yellow earth FeO(OH).

Ground 12 (Jan Vermeer): Kaolin, white lead, yellow earth FeO(OH), rabbit skin glue, stand oil.
Figure 13 shows the IR spectra of sample ground 12: stand oil is described by the two stretching bands of CH$_2$ at 2938 and 2862 cm$^{-1}$ and by the stretching band of the C=O at 1749 cm$^{-1}$. The presence of lead white is identified by the peak at 3539 cm$^{-1}$ due to the Pb(OH)$_2$ moiety and by the combination band of $\nu_1$ + $\nu_3$ at about 2403 cm$^{-1}$ due to the ((PbCO$_3$)$_2$·Pb(OH)$_2$) structure [10]. Lead white can also be identified by the distorted $\nu_3$ Reststrahlen band of CO$_3^{2-}$ around 1400 cm$^{-1}$.
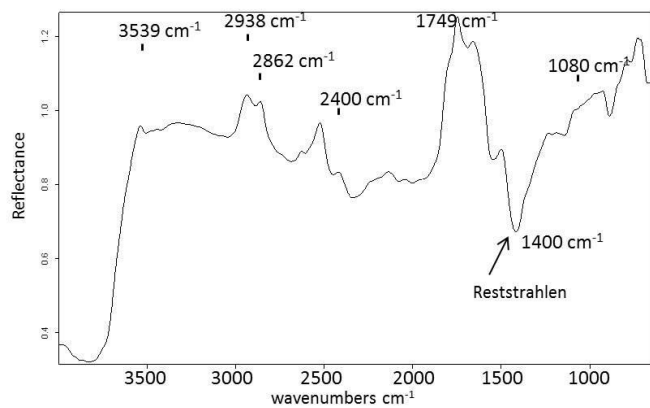At 1080 cm$^{-1}$ there is a small band attributed to the silicate of yellow earth [12].



Fig. 13: DRIFT infrared spectra of ground 12 prepared with Kaolin, white lead, yellow earth FeO(OH), rabbit skin glue, stand oil.

Ground 13 (Max Doerner): Gypsum, zinc white, rabbit skin and stand oil.
Figure 14 shows the IR spectra of sample ground 13: the strong an broad band between 3700 and 3200 cm$^{-1}$ is assigned to the anti-symmetric and symmetric O-H stretching bands of

gypsum[28]. The peak at 1674 correspond to the deformation vibrations of the O-H bond of water[7]. Due to the high adsorption index k the asymmetric SO$_4^{2-}$ stretching band of gypsum is affected by the Reststrahlen effect and consequently appears as inverted band showing the minima at about 1140 cm$^{-1}$. The enhancement of second-order and combination bands, due to diffuse reflection, is evident in the range 2500-1900cm$^{-1}$. In the reflection spectrum of gypsum both the modes $\nu_1 + \nu_3$ and $2\nu_3$ are covered by a strong and broad band at 2220 cm$^{-1}$ due to the combination of bending and vibration modes of H$_2$O [10]. Stand oil could be identified by the C-H stretching band at 2932 and 2859 cm$^{-1}$, by the stretching band of the C=O at 1750 cm$^{-1}$.
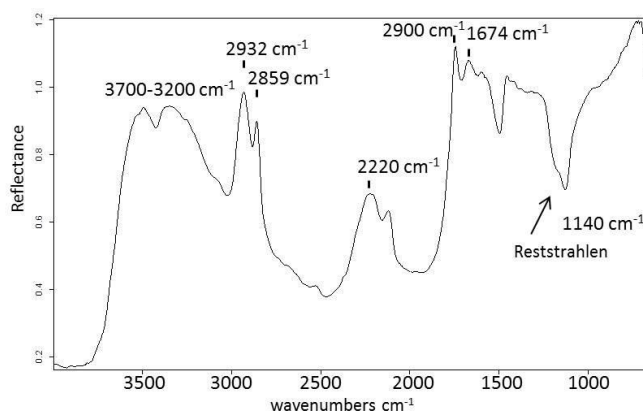


Fig. 14: DRIFT infrared spectra of ground 13 prepared with Gypsum, zinc white, rabbit skin and stand oil.

Ground 14 (Pierre Auguste Renoir): white lead, kaolin, stand oil.
Figure 15 shows the IR spectra of sample ground 14: the presence of lead white is identified by the peak at 3539 cm$^{-1}$ due to the Pb(OH)$_2$ moiety and by the combination band of $\nu_1$ + $\nu_3$ at about 2403 cm$^{-1}$ due to the ((PbCO$_3$)$_2$·Pb(OH)$_2$) structure [10]. Lead white can also be identified by the distorted $\nu_3$ Reststrahlen band of CO$_3^{2-}$ around 1400 cm$^{-1}$. Stand oil is described by the C-H stretching band at 2945 and 2865 cm$^{-1}$ and by the stretching band of the C=O at 1750 cm$^{-1}$ and by the C-O stretching band at 1180 cm$^{-1}$.
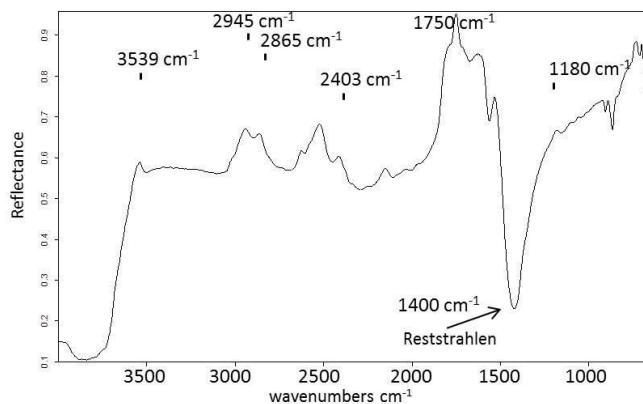


Fig. 15: DRIFT infrared spectra of ground 14 prepared with white lead, kaolin, stand oil.

Ground 15 (De Chirico): Meudon white, egg yolk, poppy oil, Venetian turpentine, white vinegar, glycerin, water.

Figure 16 shows the IR spectra of the sample ground 15: the presence of the poppy oil I identified by the two bands at 2944 and 2867 cm$^{-1}$ (stretching bands) and by the peak at 1745 cm$^{-1}$ of the stretching band of the C=O. The Meudon white (chalk) peaks related to the ν1+ν3 and ν1+ν4 bands of the carbonate anion are at 2500 cm$^{-1}$ and at 1793 cm$^{-1}$[10]. At 3400 – 3200 cm$^{-1}$ there are the N-H stretching band of the egg yolk, the C-N-H bending band is confirmed at 1562 cm$^{-1}$[7].
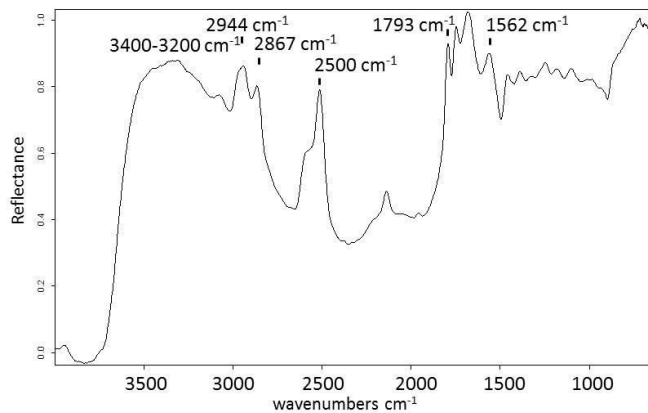


Fig. 16: DRIFT infrared spectra of ground 15 prepared with Meudon white, egg yolk, poppy oil, Venetian turpentine, white vinegar, glycerin, water.

Ground 16 (for synthetic binders): Titanium white, chalk, acrylic resin and kaolin.

Figure 17 shows the IR spectra of the sample ground 16: the acrylic resin is identified by the stretching bands of the C-H at 3100 and 2800 cm$^{-1}$, by the C=O stretching band at 1750 cm$^{-1}$ and by the C-H bending at 1464 cm$^{-1}$ and 1383 cm$^{-1}$. The detection of the inverted ν(Si-O) mode at 1020 cm$^{-1}$ coupled with a multiplet ν(OH) in the range 3700-3620 cm$^{-1}$ indicates the presence of kaolin[10, 30] The signal at 1112 cm$^{-1}$ is of the asymettric Si-O-Si stretching bend of the Kaolin[7].
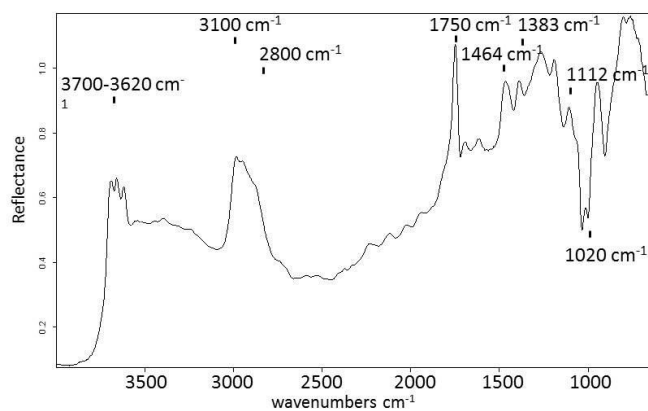


Fig. 17: DRIFT infrared spectra of ground 16 prepared with Titanium white, chalk, acrylic resin and kaolin.

Figure 18 shows the colour images of each ground analyzed by the DRIFT technique. The reference collection can be used to identify unknown canvas grounds.



Fig. 18: colour images of each canvas ground analysed by the DRIFT.

Table 2 shows the assignations of each different compounds identified. This values can be used as reference collection to identify unknown canvas grounds.

| Materials | DRIFT band assignation for each compound | | | | |
|---|---|---|---|---|---|
| Rabbit skin glue | 3500 cm$^{-1}$ | 2900 cm$^{-1}$ | 1690 cm$^{-1}$ | 1574 cm$^{-1}$ | 1464 cm$^{-1}$ |
| Gypsum | 3700 - 3200 cm$^{-1}$ | 2500 - 1900 cm$^{-1}$ | 2220 cm$^{-1}$ | 1679 - 1632 cm$^{-1}$ | 1152 cm$^{-1}$ |
| Honey | 1255 cm$^{-1}$ | | | | |
| Lead White | 3539 cm$^{-1}$ | 2400 cm$^{-1}$ | 1392 cm$^{-1}$ | | |
| Stand oil | (3400 cm$^{-1}$) 2945 - 2865 cm$^{-1}$ | 1750 cm$^{-1}$ | 1481 cm$^{-1}$ | (1374 cm$^{-1}$) | 1177 cm$^{-1}$ |
| Walnut oil | 2945 - 2968 cm$^{-1}$ | 1750 cm$^{-1}$ | 1497 cm$^{-1}$ | | |
| Linseed oil | 2925 - 2857 cm$^{-1}$ | 1742 cm$^{-1}$ | 1497 cm$^{-1}$ | | |
| Silicate | 3600 cm$^{-1}$ | 1080 cm$^{-1}$ | | | |
| Venetian Turpentine | 1395 cm$^{-1}$ | 1270 cm$^{-1}$ | 1125 cm$^{-1}$ | 1070 cm$^{-1}$ | |
| Egg | 3400 - 3200 (3309) cm$^{-1}$ | 1660 cm$^{-1}$ | 1462 cm$^{-1}$ | | |
| Poppy oil | 2944 – 2867 cm$^{-1}$ | | | | |
| Chalk | 2500 cm$^{-1}$ | 1793 cm$^{-1}$ | | | |
| Acrylic resin | 3100 - 2800 cm$^{-1}$ | 1750 cm$^{-1}$ | 1464 cm$^{-1}$ | 1383 cm$^{-1}$ | |
| Kaolin | 3700 - 3620 cm$^{-1}$ | 1112 cm$^{-1}$ | 1020 cm$^{-1}$ | | |
| Siena earth | 1112 cm$^{-1}$ | | | | |
| Raw umber | 1070 cm$^{-1}$ | | | | |

Tab. 2: assignations of each different compounds identified with DRIFT.

## Case study

The method for the non-invasive identification of the ground in canvas was used to characterize the preparation employed by the painter Guglielmo Caccia called "Il Moncalvo" in his painting "Madonna con Bambino tra San Rocco e San Michele" represented in figure 19.

Fig. 19: image of the "Madonna con bambino tra San Rocco e San Michele" from Guglielmo Caccia called "Il Moncalvo". Image taken by the author during the analysis at the Studio Rava.

The analysis was carried out pointing the infrared beam on the ground surface to the side of the frame as shown in figure 20a. Often, ground measurements can be performed on the back of the painting: ground tends to pass through the canvas and if the back was not cleaned or brushed it can be detected (figure 20b).



Fig 20: portable DRIFT at work on two different canvas: (a) on the side and (b) on the back of the canvas. Images taken by the author during the analysis at the Studio Rava.

Figure 21 shows the infrared spectra of the measured ground of the Moncalvo's painting: comparing the spectra with the reference collection of the grounds previously developed it was possible to identify the composition of the ground used by the artist. The painter used the preparation identified as ground 2

made by gypsum, animal glue and honey. The strong an broad band between 3700 and 3200 $cm^{-1}$ is assigned to the anti-symmetric and symmetric O-H stretching bands of gypsum[7], the peaks at 1679 and 1632 $cm^{-1}$ are the deformation vibrations of the O-H bond of water[28] and were assigned to gypsum. Due to the high adsorption index k the asymmetric $SO_4^{2-}$ stretching band of gypsum is affected by the Reststrahlen effect and consequently appears as inverted band showing the minima at about 1152 $cm^{-1}$. The enhancement of second-order and combination bands, due to diffuse reflection, is evident in the range 2500-1900 $cm^{-1}$. In the reflection spectrum of gypsum both the modes $v_1 + v_3$ and $2v_3$ are covered by a strong and broad band at 2220 $cm^{-1}$ due to the combination of bending and vibration modes of $H_2O$ [10] . Near 2900 $cm^{-1}$ there are the C-H stretching bands of the rabbit skin glue. The signal at 1258 $cm^{-1}$ is assigned to the honey [10].The results are confirmed by the conservator: in fact the painter is from the XVI century when the most used grounds in that period were made of gypsum and animal glue.
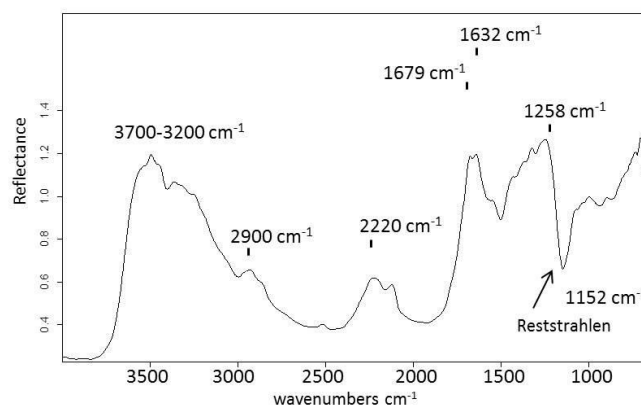


Fig. 21: DRIFT spectra of the Moncalvo's painting: the analysis revealed that the painter used gypsum and animal glue as ground.

## Conclusions

A portable diffuse reflectance infrared Fourier transform (DRIFT) method for the non-invasive characterization of the ground in paintings was presented: with this method there is no need to touch the sample and the analysis can be performed directly on site.

Sixteen of the most important canvas grounds, used by artist from XIV to XX century like Vasari, Mantegna, Veronese, Caravaggio and De Chirico, were prepared and analyzed using DRIFT in order to build a unique reference library of spectra. Most of the main band were identified. Furthermore, the Infrared library can be used as reference database also in conjunction with other IR spectroscopy methods, even if we must state that changes in the relative proportions of ground materials in real artworks may promote a DRIFT spectra "different" in form and shape to the spectra proposed as standard. However, the wavelengths of the maximum of the infrared bands, can be used as indicative of given compounds because they never change when the relative proportions among compounds change in the unknown samples. The DRIFT spectra gives important information to unequivocally identify typical compounds that could be present in the ground layer of any canvas painting.

The DRIFT spectra of the ground of a Moncalvo's painting was measured in order to identify the type of ground that was used. Comparing the spectra with the reference collection was possible to easily identify the composition of the ground used by the artist that resulted constituted by gypsum, animal glue and honey. Moreover, the results were confirmed by the conservator: in fact the painter is from the XVI century when the most used grounds were made by gypsum and animal glue. Although the technique used in this study is non-invasive, an area with some canvas ground exposed is needed in order to analyse it. The use of a DRIFT handled device could be a valid alternative to the Raman spectroscopy for the non-invasive characterization of cultural heritage materials.

## Acknowledgements

## Notes and references

[a] Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, viale Teresa Michel, 11 – 15121, Alessandria, Email: marcello.manfredi@unipmn.it; Tel. +393334722270

[b] Centro Conservazione e Restauro La Venaria Reale, via XX Settembre 18, 10078, Venaria Reale (TO).

[c] ISALIT S.r.l., Via G. Bovio 6, 28100, Novara (NO).

1   F. Casadio and L.J. Toniolo, *Journal of Cultural Heritage*, 2001, **2**, 71–78.

2   E. Marengo, M.C. Liparota, E. Robotti, M. Bobba, *Vibrational Spectroscopy*, 2006 , **40(2)**, 225-234.

3   E. Robotti, M. Bobba, A. Panepinto, E. Marengo, *Analytical and Bioanalytical Chemistry,* 2007, **388 (5-6)**, 1249-1263.

4   Z. Kaszowska, K. Malek, M. Pańczyk and A. Mikołajska, *Vibrational Spectroscopy*, 2013, **65**, 1-11.

5   A. Bonizzoni, S. Caglio, A. Galli and G. Poldi, Applyed Physics A, 2008, **92**, 203–210.

6   M.R. Derrick, D. Stulik and J.M. Landry, *Infrared Spectroscopy in Conservation Science*, The Getty, Los Angeles, 1999.

7   M.J.D. Low and N.S. Baer, *Stud. Conserv.,*1977, **22**, 116–128.

8   E. Joseph, C. Ricci, S.G. Kazarian, R. Mazzeo, S. Prati and M. Ioele, *Vibrational Spectroscopy*, 2010, **53**, Issue 2, 274-278.

9   G. Sciutto, P. Oliveri, S. Prati, M. Quaranta, S. Lanteri, R. Mazzeo, *Analytical Bioanalytical Chemistry*, 2013, **405**, 625–633.

10  C. Miliani, F. Rosi, A. Daveri, B.G. Brunetti, Applied Physics A, , 2012, **106**, 295-307.

11  C. Miliani, F. Rosi, B.G. Brunetti, A. Sgamellotti, *Accounts of Chemical Research*, 2010, **43 (6)**, 728-738.

12  F. Rosi, C. Miliani, C. Clementi, K. Kahrim, F. Presciutti, M. Vagnini, V. Manuali, A. Daveri, L. Cartechini, B.G. Brunetti, A. Sgamellotti, *Applied Physics A*, 2010, **100**, 613-624.

13  W. Vetter, M. Schreiner, *e-PRESERVATIONScience*, 2011, **8**, 10-22.

14  N. Navas, J. Romero-Pastor, E. Manzano, C. Cardell, *Analytica Chimica ACTA*, 2008, **630**, 141-149.

15  L. Monico, F. Rosi, C. Miliani, A. Daveri, B.G. Brunetti, *Spectrochimica ACTA Part A: Molecular and Biomolecular Spectroscopy*, 2013, **116**, 270-280.

16  M. Fabbri, M. Picollo, S. Porcinai, M. Bacci, Applied Spectroscopy, 2001, **55(4)**, 138-152

17  I. Arrizabalaga, O. Gomez-Laserna, J. Aramendia, G. Arana, J.M. Madariaga, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* 2014, **129**, 259-267.

18  C. Maltese, Preparazione e finitura delle opere pittoriche, Mursia Editore, Milano, 1993.

19  Bettarini (a cura di), Vasari, introduzione alle tre arti del disegno cap. XXIII, "Della pittura", Edizione Barocchi, 1966, pp. 136, 137.

20  Gorreri (a cura di), Armenini (1586), "De'veri precetti della pittura", Einaudi, Torino, 1988, cap. IX, p. 143.

21  D.M. Pagano (a cura di), testi di D.M. Pagano, B. Arciprete, M. Cardinali, Caravaggio a Napoli dalle opere di Misericordia alla Sant'Orsola trafitta: tecnica e restauri, Electa, Napoli, 2005.

22  S. Rinaldi (a cura di), T.T. De Mayerne, Pittura e scultura delle arti minori: 1620-1646: Ms. Sloane 2052 del British Museum di Londra, in Letteratura artistica. Collana diretta da Fabio Benedettucci. Vol. 3, De Rubeis, Nettuno, 1995, p. 220.

23  M.P. Merrifield (a cura di), Giovanni Battista Volpato, Modo da tener nel dipinger, Original treatises on the art of painting, London, 1849, vol. II, p. 729.

24  S. Rinaldi (a cura di), T.T. De Mayerne, Pittura e scultura delle arti minori: 1620-1646: Ms. Sloane 2052 del British Museum di Londra, in Letteratura artistica. Collana diretta da Fabio Benedettucci. Vol. 3, De Rubeis, Nettuno, 1995, pp. 120-121.

25  M. Doerner, The Materials of the Artist and Their Use in Painting, with Notes on the Techniques of the Old Masters, Granada Publishing, London, 1977, pp. 23-27.

26  D. Bernar, I capolavori di Pierre Auguste Renoir, Fabbri Editore, Milano, 1988.

27. De Chirico, Piccolo trattato di tecnica pittorica, Vanni Scheiviller Editore, Milano, 1928.28

28  C. Genestar, Materials Letters, 2002, **54**, 382-388.

29  T. Gatta, L. Campanella, C. Coluzza, V. Mambro, P. Postorino, M. Tomassetti, G. Visco, Chemistry Central Journal, 2012, **6(2),** S2.30

30  C. Miliani, F. Rosi, A. Burnstock, B.G. Brunetti, A. Sgamellotti, Applied Physics A, 2007, **89**, 849-856.

31. J. Van der Weerd, A. van Loon, J. J. Boon, *Studies in Conservation,* 2005, **50**, 3-22.