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# New Advances in the Application of FTIR Microscopy and Spectroscopy for the Characterization of Artistic Materials

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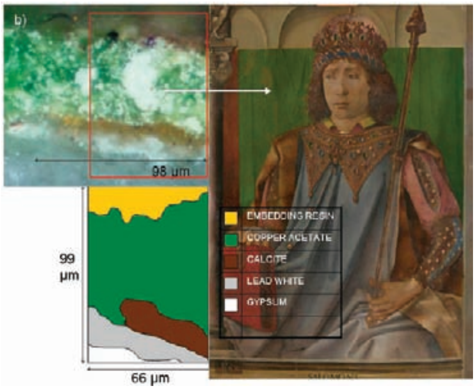
## CONSPECTUS



Fourier transform infrared (FTIR) spectroscopy is one of the most widely applied techniques for the investigation of cultural heritage materials. FTIR microscopy is well established as an essential tool in the microdestructive analysis of small samples, and the recent introduction of mapping and imaging equipment allows the collection of a large number of FTIR spectra on a surface, providing a distribution map of identified compounds.

In this Account, we report recent advances in FTIR spectroscopy and microscopy in our research group. Our laboratory develops, tests, and refines new and less-studied IR spectroscopy and microscopy methods, with the goal of their adoption as routine analytical techniques in conservation laboratories. We discuss (i) the analysis of inorganic materials inactive in the mid-IR region by means of far-IR spectroscopy, (ii) the development of new methods for preparing cross sections, (iii) the characterization and spatial location of thin layers and small particles, and (iv) the evaluation of protective treatments.

FTIR spectroscopy and microscopy have been mostly used in the mid-IR region of 4000−600 cm$^{-1}$. Some inorganic pigments, however, are inactive in this region, so other spectroscopic techniques have been applied, such as Raman spectroscopy. We suggest an alternative: harnessing the far-IR (600−50 cm$^{-1}$). Our initial results show that far-IR spectroscopy is exceptionally useful with mural paintings or with corrosion products from which larger sample quantities can generally be collected. Moreover, the inorganic composition of a sample can be characterized by the presence of several compounds that are inactive in the mid-IR range (such as sulfides, oxides, and so forth).

Stratigraphical analyses by FTIR microscopy can be hindered by the process of cross section preparation, which often involves an embedding organic polymer penetrating the sample's porous structure. Here, the polymer bands may completely cover the bands of organic compounds in the sample. However, a correct methodological approach can prevent such limitations. For example, it is always advisable to analyze the sample surface before preparing the cross section in order to characterize the preparation layers and the varnish layers, which are generally applied to the surface of a painting both to protect it and improve the color saturation. Furthermore, the innovative use of IR-transparent salts as embedding material for cross sections can prevent contamination of the embedding resin and improve detection of organic substances.

Another key point in the use of FTIR microscopy in artwork analysis is spatial resolution. The high-energy output of a new integrated FTIR microscope enhances the ability to characterize and spatially locate small particles and thin layers. Moreover, the new configuration proves extremely useful in the evaluation of protective treatments, because larger areas may be analyzed in less time in comparison to traditional systems, allowing the collection of more statistical data.

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## 1. Introduction

Chemistry was first applied to the conservation field in the 18th century, gradually assuming a fundamental role, due to the increased number of collections exhibited in the museums of Europe.[1] Presently, chemistry for cultural heritage is employed to determine the nature of ancient materials, reveal production techniques and usage, support archaeometric studies (provenance, datation, attribution), detect causes and mechanisms of degradation, as well as develop and evaluate methods of restoration.[2]

Works of art are often composed of different layers. Each layer is a mixture of different compounds (i.e., pigments, binders). Moreover, the overall composition can change with time, leading to the formation of degradation products. Such matrices are not easy to be studied, given the difficulties to physically separate the different thin layers (less than 1 $\mu$m up to 200 $\mu$m). Another issue is that in this field it is of outmost importance to reduce the number and amount of samples taken from the object. For this reason, it is recommended to follow a methodological approach where nondestructive and microdestructive techniques can combine in an integrated way.

Nondestructive techniques alone (X-ray radiography, X-ray fluorescence (XRF), multispectral imaging system, portable Fourier transform infrared spectroscopy or Raman) cannot provide a detailed stratigraphical characterization of the samples. However, they are extremely useful, because they allow chemical dishomogeneity of the artworks to be documented, thus providing a better identification of the areas to be sampled.

Infrared (IR) spectroscopy in the mid-IR range (4000−600 cm$^{-1}$) is one of the most widely applied techniques for the investigation of cultural heritage materials.[3,4] When microsampling accessories for Fourier transform infrared (FTIR) spectroscopy were introduced in the early 1980s, the subsequent development of FTIR microscopy became an essential tool in the microdestructive analysis of small samples.[5] Furthermore, the recent introduction of mapping and imaging equipment allows one to collect a large number of FTIR spectra on a surface and to produce a distribution map of the identified compounds.

This Account reports the recent advances of FTIR spectroscopy and microscopy in artwork diagnostics achieved by our research group. Our research activities are aimed at developing, testing, and experimenting new and less studied infrared spectroscopy and microscopy methods to be eventually adopted as routine scientific analysis in conservation laboratories.

## 2. State of the Art of the Instrumentation Employed in the Cultural Heritage Field

Analysis by FTIR spectroscopy and microscopy may be accomplished in several ways, depending on the amount and on the type (powder or fragment) of the available samples. Figure 1 shows different analytical approaches depending on the nature of the sample.

**2.1. FTIR Spectroscopy.** FTIR analyses can be performed in transmission with the IR radiation passing through the sample. This method benefits of a high energy throughput and a resulting high sensitivity. Samples are dispersed in IR inactive powder materials and prepared as pellets or as thin films between IR transparent windows.

Opaque samples can be analyzed in reflectance without any preparation. This method is based on the principle that when an incident radiation passes through two different media, it is split into reflected and transmitted beams in different proportions according to the refractive index ratio of the two materials.[6] When the analyzed surface is not totally reflecting, the resulting spectra can be difficult to be interpreted due to the presence of diffuse reflection, refraction, or scattering. In order to obtain spectra more similar to those obtained in transmission, macro attenuated total reflection (ATR) can be used. A crystal (IRE, internal reflection element) with a higher refractive index than the sample is put in contact with it. Total reflection is produced when the incident radiation passes from the IRE to the sample with a particular incidence angle, called the critical angle. When the incident angle is greater than the critical one, an evanescent wave forms up on the surface of the IRE and can penetrate the sample which is optically less dense, resulting to be attenuated.

Both in reflection and in transmission, analyses of artistic materials have been so far performed mainly in the mid range (4000−600 cm$^{-1}$). Only a few research studies from the early 1970s report the use of far-infrared spectroscopy (600−50 cm$^{-1}$)[7,8] on inorganic compounds. The limited attention paid to this technique is probably due to the enormous advantages provided by Raman spectroscopy in terms of high spatial and spectral resolution. Portable Raman and microscopes have been developed and widely employed for the characterization of pigments in artworks.[9,10] However, an inconvenience of Raman spectroscopy is fluorescence emissions, sometimes masking the Raman signal,[9] even though new approaches have been developed.[10] For these reasons, provided that an

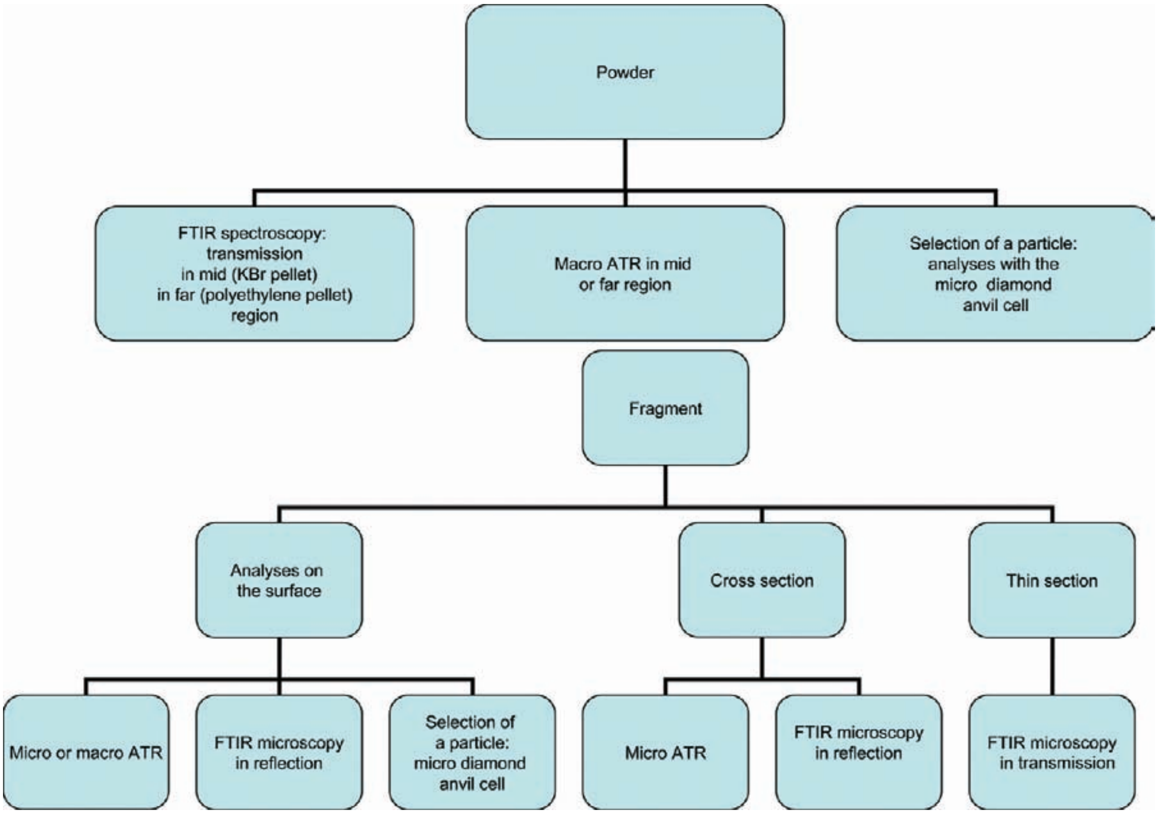

**FIGURE 1.** Scheme of the possible analysis in FTIR spectroscopy and microscopy on powder or fragments.

adequate amount of sample is available, far-IR spectroscopy represents a complementary technique to detect inorganic compounds that are not active in the mid region in fluorescent organic media.[11−14]

**2.2. FTIR Microscopy.** A FTIR microscope consists of a FTIR spectrometer combined with an optical microscope. The latter embodies all-reflecting optics and aspherical surfaces, adapted to the infrared radiation to minimize optical aberrations.

The microscope spatial resolution is a crucial element in the application of this technique in the field of cultural heritage in order to characterize thin layers or small particles. Using a single-element mercury cadmium telluride (MCT) detector, the spatial resolution is related to the infrared beam aperture dimension which cannot be lower than the theoretical diffraction limit of about 10 $\mu$m. However, it is difficult to obtain a good signal-to-noise ($S/N$) ratio with such aperture dimension, and therefore, at least 20 × 20 $\mu$m aperture is needed to obtain enough energy.[15]

FTIR microscopy in transmission is suitable on small particles or on thin film employing IR transparent materials as support (i.e., NaCl window).[16] Microparticles can be analyzed with the diamond anvil cell, a simple device that can be placed directly on the stage of a FTIR microscope. The particle is placed onto a microcompression cell made of diamond and pressed in order to squeeze it. It is particular useful for the analysis of single organic colorant particles, especially when they are mixed with strong absorbent inorganic salts and organic binders to reduce the influence of other components.[17] Recently, the diamond anvil cell has also been proposed for the study of multilayered samples.[18] After careful positioning on a diamond window followed by compression, the sample stratigraphy can be preserved with only an expansion of each individual layer. Transmission measurements can also be performed on thin sections obtained after polishing or microtoming an embedded cross section. However, the preparation of thin sections of artistic polimaterial samples is a difficult task. Even though procedures based on microtomy have been proposed as standard methods, the possible presence of materials with different hardness may produce an easy deformation of the section, with subsequent particle loss and curling. Alternative methods, that is, using IR transparent salts such as silver chloride (AgCl) or potassium bromide (KBr),[19−21] still have some limitations, such as darkening or accelerated corrosion for AgCl.

Reflection methods have been successfully employed for the analysis of either the sample surface or its cross section.[22] However, as reported above, the resultant spectra may be of difficult interpretation when the sample surface is not totally reflecting. For paint cross sections, the surface quality can be improved using adequate mechanical polishing methods or advanced techniques, such as an ion milling system or focused ion beam.[23]

Reflection−absorption measurements can be performed when a thin film (not more than 15 $\mu$m) is laid on a metal surface. In such conditions, the IR radiation passes through the sample and is reflected back by the metal surface, yielding high-quality spectra comparable to those registered in the transmission mode. However reflection−absorption spectrometry (RAS) can be applied only in some restricted cases, such as the study of protective coatings on metal artworks[24] or for the characterization of varnish layers on gilded art objects.

Attenuated total reflection (micro ATR) is widely employed in FTIR microscopy. An important advantage of ATR investigation is that it allows the investigation of smaller areas maintaining the same aperture, thanks to the magnification factor of the IRE.[25] As an example, the actual investigated area is 25 $\mu$m × 25 $\mu$m, with an aperture of 100 $\mu$m × 100 $\mu$m and an IRE of germanium (refractive index = 4). The main drawback of this method is that the spectral quality may be negatively affected if the contact between the IRE and the sample is not adequate. Therefore, also in this case sample preparation is of outmost importance.

In the last decades, FTIR microscopy performance has been improved by the introduction of mapping and imaging equipment, allowing to collect a large number of FTIR spectra and to assemble a pattern showing the distribution of different compounds.[22,26−29]

FTIR mapping systems produce sequential data collection using a single-element MCT detector, adjustable apertures to select the investigated area, and a motorized stage. The spatial resolution is related to the aperture dimensions and to the acquisition method (reflection, transmission, or ATR), as mentioned above. The main disadvantage of the mapping system is the long time required for acquisition (hours).

FTIR imaging consists of a simultaneous, and therefore faster, data collection performed by a multichannel detector where small pixels of about 6 $\mu$m are distributed over a grid pattern (FPA, focal plane array).[26,27] This kind of detector allows the recording of the optical signal's entire field of view (FOV) and requires no aperture. Typical IR sensitive focal plane array (FPA) detectors include 64 × 64, 128 × 128, and 256 × 256 elements (pixels) arranged in a regular pattern. Compared to the mapping system, where geometrical apertures are used, the spatial resolution is in this case determined by the pixel dimension. Unfortunately, this causes also a poor spectral quality (low signal-to-noise ratio or *S*/*N*) since the photon quantity received by each pixel is in inverse proportion to the number of pixels. For large detectors, this means low photon quantity. The cutoff of the focal plane array detector at 900 $cm^{-1}$ is a significant disadvantage in distinguishing several inorganic compounds with characteristic absorption down to 650 $cm^{-1}$ (i.e., calcite and lead white).

Linear array detectors (raster scanning) have been recently developed combining several MCT detectors with a motorized stage to sequentially scan lines. This system reduces the acquisition time by a factor corresponding to the number of detector elements. The size of the individual elements is 25 $\mu$m, permitting one to obtain spectra with a good spectral quality. In transmission or reflection mode, the achieved resolution of 25 $\mu$m can be reduced to 6.25 $\mu$m using an optical zoom, while in ATR the spatial resolution is reduced by the crystal magnification (~6 $\mu$m with a germanium crystal).

In recent times, a new integrated FTIR microscope has been designed, offering the powerful combination of a microscope with an incorporated FTIR spectrometer (interferometer, source, laser, and detector). The main advantage of this setting is the higher energy compared to conventional systems, where energy losses are due to the radiation optical path from spectrometer to microscope. One of our recent studies shows how this new configuration can increase the system spatial resolution maintaining a good spectral quality.[28]

The new setting is not comparable with systems coupled with synchrotron light, but it may be an alternative for the characterization of particles and layers down to 10 × 10 $\mu$m when the synchrotron radiation (SR) facilities are not accessible. SR light, thanks to its high brightness and collimation, allows spatial resolution down to 5 $\mu$m × 5 $\mu$m and may be employed in transmission or reflection.[18,30]

## 3. Application of Far-IR Spectroscopy

As previously mentioned, the far-infrared (FIR) spectral region has been less investigated than the mid infrared (MIR) in the cultural heritage field, even though it provides great advantages in the characterization of inorganic compounds inactive in the MIR, such as some art pigments, corrosion products, and so forth. Furthermore, FIR spectroscopy is complementary to Raman spectroscopy when considering the fluorescence effects which may affect the latter.

That is the reason why our research group has paid particular attention to the FIR option and has developed analytical methodologies for its application in the conservation field.[11,12] Transmission can be performed on powder after embedding the sample in polyethylene. The preparation of the pellet requires heating up to 180 °C in order to melt the polyethylene. Several tests have been performed to maximize the signal output paying attention to the preparation of the sample in order to obtain an enough IR transparent pellet. Another important factor is the effect of heating on the investigated pigments/minerals. So far, no effects have been evidenced, but our opinion is that such a pretreatment may affect organic substances. In order to avoid the thermal treatment and decrease the sample amount needed for the analysis, macro ATR based on a diamond IRE has been tested.[12−14] A few grains (around 0.1−0.5 mg) of pigment can in fact be easily and rapidly analyzed without any sample preparation. As expected, ATR spectra, when compared with transmission, presented band distortions with particular changes in intensity and shifts to lower frequencies. Both methodologies have been tested on real samples with interesting results.

## 4. Development of New Cross Section Preparation Methods

Stratigraphical analyses by means of FTIR microscopy can be negatively affected by the cross section preparation which implies the use of an embedding organic polymer often penetrating into the sample porosity. When this happens, the polymer bands may completely cover other organic compound bands.

A correct methodological approach can prevent such limitations. For instance, the analysis of the sample surface before the preparation of the cross section is always advisible for the characterization of preparation layers and the analysis of external varnish layers.[29]

The use of infrared transparent salts as embedding material for cross sections has been introduced in order to avoid the contamination of the embedding resin and to improve the detection of organic substances.[21,29] A first attempt with the use of potassium bromide (KBr), which is commonly employed for the preparation of transmission pellets, has given very promising results. In a previous publication,[29] we showed how simple is the procedure to obtain cross sections and how the detection of organic substances can be therefore improved. In addition, the KBr embedding system also leads to better observations of paint cross sections under ultraviolet illumination, thanks to the absence of the embedding resin fluorescence contribution.

However, KBr is a very hygroscopic material and the spectral quality is reduced during the acquisition, particularly during the first 20 min of FTIR measurements. Therefore, other infrared salts with a minor hygroscopicity were investigated, such as calcium fluoride ($CaF_2$) and barium fluoride ($BaF_2$) (Table 1).

**TABLE 1.** Solubility of Infrared Optics Materials

| IR material | solubility (g/100 g $H_2O$) |
|---|---|
| KBr | 53.5 |
| $CaF_2$ | 0.0013 |
| $BaF_2$ | 0.17 |

A standard paint reconstruction, composed of a preparation layer (gypsum and glue) and a painting layer (malachite and oil), has been used to evaluate the performance of the different salts as embedding media. For both $CaF_2$ and for $BaF_2$, the embedding procedures were adapted to compact the salts in pellets. Nevertheless, the results achieved with $CaF_2$ were not successful, as the paint fragment embedded into it was not visible. The signal-to-noise ratio (*S/N*) value between 4000 and 3800 cm$^{-1}$ was measured during 2 h of time, mapping an area on the preparation layer of similar paint fragments embedded in either KBr or $BaF_2$ (Figure 2). For each data set obtained, the peak-to-peak noise, available on each FTIR elaboration software, was measured between 4000 and 3800 cm$^{-1}$ at 10 min intervals and the S/N calculated as follows:

$$S/N = 1/(1-10^{-N})$$

The $BaF_2$ embedded sample shows, after about 60 min, a rather low improvement of the spectral quality in respect to KBr, and furthermore, the pellet appears to be more fragile. Hence, KBr cross sections provide the best result so far achieved. The method may be further improved by controlling the atmosphere under the FTIR microscope stage during measurements. Moreover, the polishing procedure is still a delicate step because KBr is more fragile than an organic resin. At present, our group is committed to finding new systems and devices to standardize the procedure in order to improve the sample planarity.

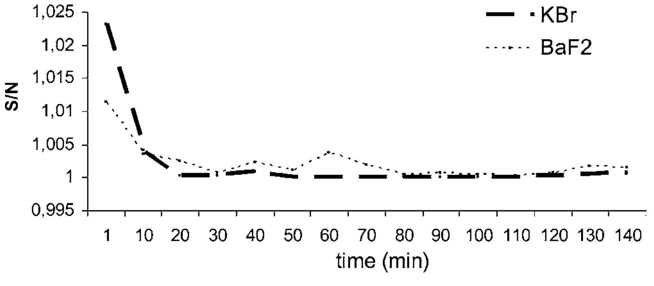

**FIGURE 2.** Variation of the signal-to-noise ratio (*S/N*) with time measured in FTIR spectra acquired on the preparation layer of a malachite paint reconstruction embedded in KBr or $BaF_2$.

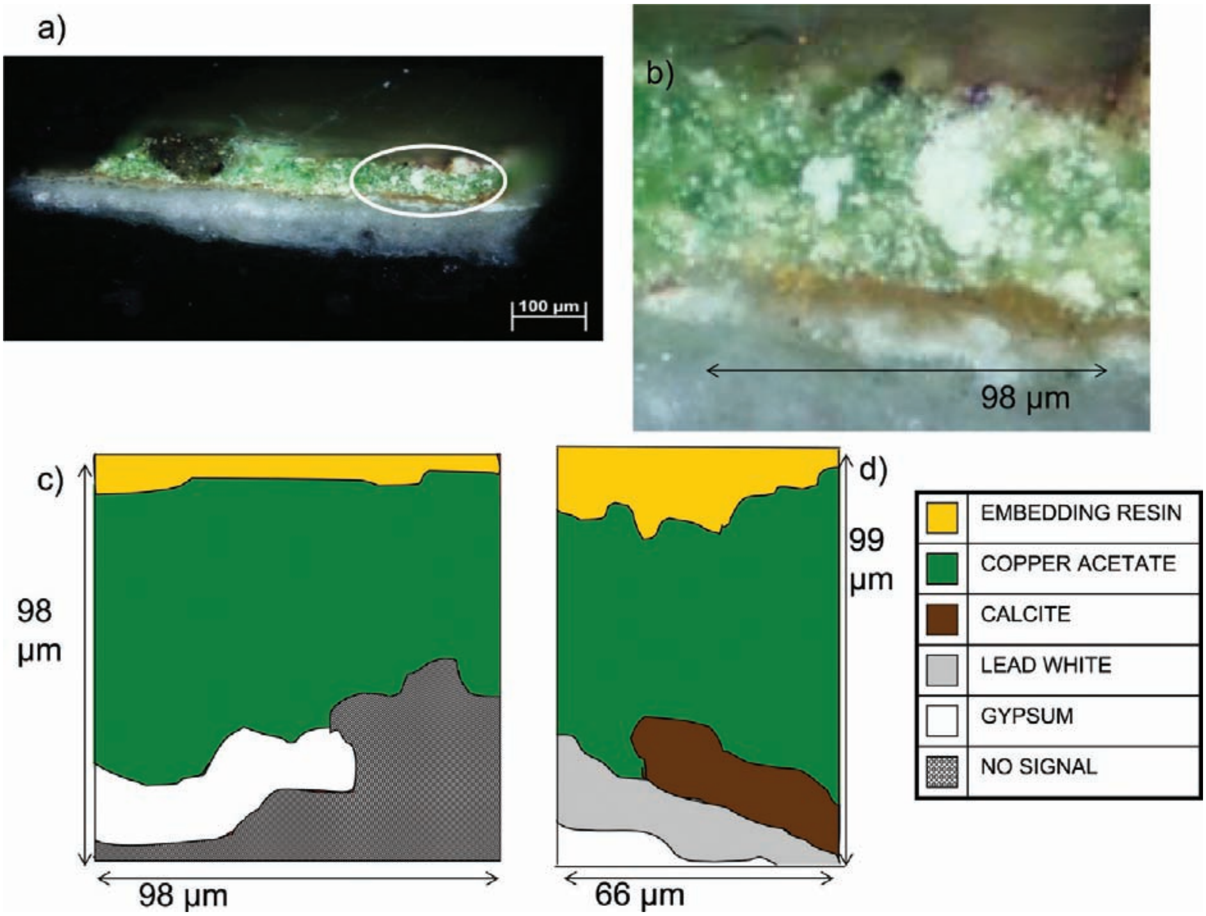

**FIGURE 3.** (a) Cross section photomicrograph of a green sample from the Salomone portrait with the indication of the area investigated; (b) same cross section photomicrograph taken at higher magnification indicating the area investigated with FTIR microscopy; (c) composition scheme of the sample obtained by mapping FTIR in ATR with a traditional microscope (aperture 80 × 80 $\mu$m, scans 64); (d) Composition scheme of the sample obtained by mapping FTIR in ATR with the integrated microscope (aperture 20 × 20 $\mu$m, scans 16).

## 5. Characterization of Thin Layers and Small Particles

Sometimes artistic samples can be characterized by the presence of complex multilayers whose thickness ranges from 1 to 100 $\mu$m. Therefore, the spatial resolution of the employed analytical setup is of outmost importance in the characterization of thin layers and small particles that can be dispersed with other substances into each layer.

To optimize the spatial resolution, our research activities have focused on ATR, because the investigated area is reduced thanks to the magnification factor of the IRE. We already showed[29] that compounds with strong and characteristic absorption can be detected even when they are present in layers thinner than the spatial resolution. The distribution, however, does not fit with the real dimension of the layer.

Using the integrated FTIR microscope, it is possible to obtain a spatial resolution down to about 6 $\mu$m. Within this limit, the distribution map matches the real layer thickness. Moreover, due to the integrated configuration adopted, the spectral quality is preserved. Figure 3 shows the results obtained on a green paint sample collected from the Salomone portrait (Uomini Illustri portraits, attributed to Juste de Gande and Pedro Berruguete, end of 15th century, Ducal Palace, Urbino, Italy). The schemes of the different compounds' mapping distribution obtained in two similar areas of the sample show that, with the integrated system (aperture 20 × 20 $\mu$m, 16 scans, Thermo iN10MX instrument), even with a slightly lower aperture and a number of scans lower than that of the conventional apparatus (aperture 80 × 80 $\mu$m, scans 64, Thermo Continuum instrument), it is possible to map very thin layers of lead white and calcite (10−14 $\mu$m). In fact, with the conventional apparatus, it was not possible to further reduce the aperture without negatively affecting the signal and, in the selected conditions, the achieved spatial resolution does not allow detection of the above-mentioned thin layers.

Figure 4 shows another interesting application of the integrated microscope. The improved spatial resolution, achieved

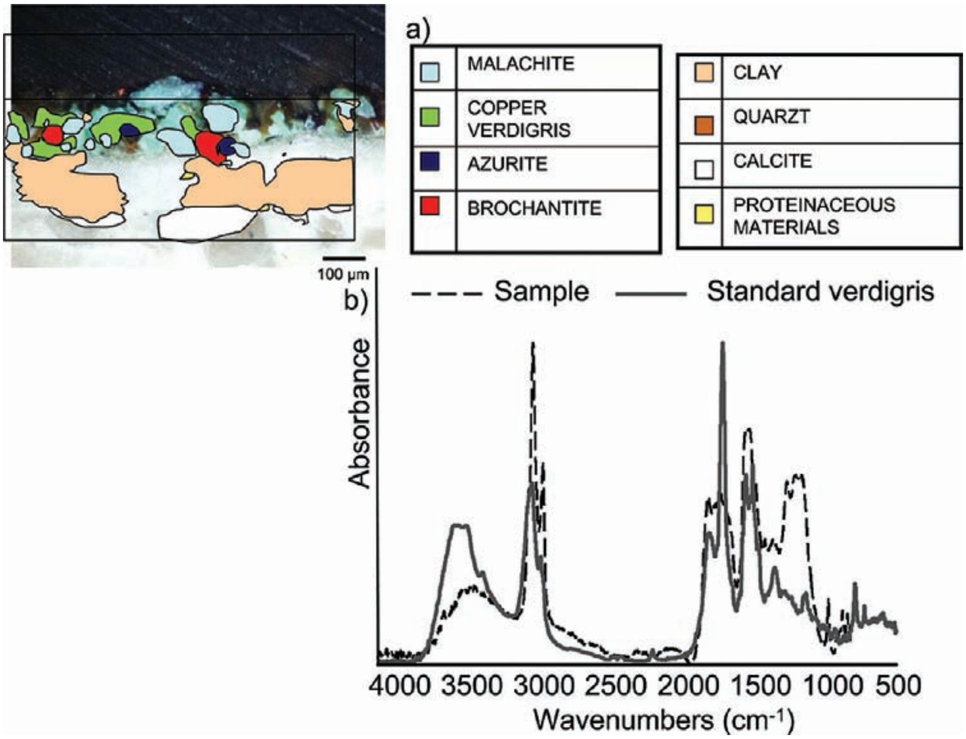

**FIGURE 4.** (a) Composition of T2 sample as obtained by raster scanning analyses; (b) spectra of a green area indicating the presence of copper carboxylates and of a standard verdigris (spectrum registered in transmission).

without affecting the spectral quality, provided a more detailed characterization of the different layers' composition. A green sample (T2) belonging to a decoration collected from the Thubchen Lhakhang temple mural paintings (15th century) located in Lo Manthang, Nepal, was analyzed with raster scanning mode (Thermo iN10MX instrument). Mapping experiments with a traditional FTIR microscope (Thermo Continuum instrument, aperture 150 × 150 and 64 scans) allowed the identification, within the painted layer, of malachite and of an organic binder that could be attributed to a highly degraded siccative oil.[29] Raman analyses on a green sample, similar to T2 and collected from the same temple,[31] helped in detecting the presence of azurite and brochantite, besides malachite. Raster scanning analyses confirmed in sample T2 the same composition found in the other green sample. Furthermore, the distribution map seemed to match to each single pigment particle shape (Figure 4a).

Thanks to the improved spectral quality, the integrated system allowed to obtain more information in the region 1700−1500 $\mathrm{cm}^{-1}$. The two large bands at around 1600 and 1420 $\mathrm{cm}^{-1}$ suggest the presence of copper acetate (symmetric and asymmetric stretchings of the acetate bond, respectively).[32] Figure 4 shows that the spectrum well matches a copper verdigris profile (pigment purchased by Zecchi). The high content of free fatty acids together with the 1255 $\mathrm{cm}^{-1}$ band suggests the contemporary presence of a natural resin that can be also associated to the presence of a copper resinate pigment. It is not known whether copper resinate, widely employed for easel paintings in Northern Europe and Italy since the 15th and 16th centuries, was used in Nepal, too. A shoulder at 1581 $\mathrm{cm}^{-1}$ suggests the presence of other copper carboxylates such as the ones deriving from the interaction between a copper based pigment and the fatty acids of a siccative oil.[33] For this reason, the contemporary presence of a natural resin and an oil cannot be excluded.

## 6. Application of FTIR Microscopy for the Evaluation of Protective Treatments

In previous publications, it has been reported how FTIR-ATR microscopy offers new analytical possibilities to monitor the formation and the localization of degradation products[33,34] and to study the penetration of protective treatments in stones.[35] In this section, we describe the application of FTIR microscopy in raster scanning mode for the evaluation of the distribution of protective products applied on corroded bronzes, in order to evaluate their performance. The aim is to propose new conservation approaches for outdoor exposed bronzes, considering the coexistence of corrosion products with different stability. The deterioration of outdoor bronze artifacts is the result of complex interactions with the surrounding environment, leading to a wide variety of corrosion

**TABLE 2.** Composition of Natural and Artificial Patinas

| sample name | description | composition |
|---|---|---|
| UA | urban artificial (obtained with the Pichler process on bronze coupons) | antlerite $Cu_3SO_4(OH)_4$ with traces of brochantite $Cu_4(OH)_6SO_4$ |
| UN | urban natural (copper roof exposed in Munich for 30 years) | brochantite $Cu_4(OH)_6SO_4$ |
| MN | marine natural (bronze coupons exposed in Cabo Raso for 1 year) | atacamite $Cu_2Cl(OH)_3$ with traces of phosphates, silicates, and malachite $Cu_2CO_3(OH)_2$ |

products.[36] The most common approach so far adopted is to apply organic coatings traditionally used by industrial activities, but without adapting materials and methods to specific inhomogeneous and corroded surfaces.

Two fluoroalkylsilanes Dynasylan F8263 (triethoxy-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl) silane ready-to-use solution in isopropanol, T1S) and Dynasylan SIVOCLEAR (bicomponent of fluoroalkylsilane K1 in isopropanol and catalyst K2, T2S) (Chemspec, Degussa) were tested with the aim of verifying their performances on standard bronzes with different patina compositions. These products are usually employed as consolidants on stone, thanks to their capability to form Si−O−Si bonds with the Si−OH groups. In this case, we show how micro FTIR can be employed becoming a fundamental step of the analytical protocol for the evaluation of treatment performances. Specific publications providing more details about mechanisms and performances of the exposed treatments are being prepared.

Standard bronze coupons (70 × 50 × 2.5 mm$^3$, 85% copper, 5% tin, 5% lead, and 5% zinc), artificially and naturally aged in order to obtain typical urban or marine corrosion patinas (see Table 2 for their compositions), were treated with the different protectives and either exposed again in marine or urban-marine environments for 18 months, or artificially aged until reaching 2000 h of aging.[37,38]

Several analytical techniques, such as electrochemical impedance spectroscopy (EIS), colorimetry, thickness measurements, X-ray difraction (XRD), and scanning electronic microscopy/energy dispersive X-ray (SEM-EDX), were carried out at each stage in order to understand the protective performances as compared with standard treatment (Incralac).[39]

The main result achieved concerns the effectiveness of the two fluorinated silanes in both protecting and inhibiting corrosion when compared with the presently used double-layer protective coating, made by combining acrylic resin, onto which a further microcrystalline wax layer is applied. The coupons surfaces were characterized by micro FTIR measurements in reflection mode with the integrated microscope Thermo iN10MX before and after the treatment. The presence of fluorinated silanes was identified at 1239 cm$^{-1}$ ($\nu_{as}CF_2$; $\rho CF_2$) and 1206 cm$^{-1}$ ($\nu_{as}CF_2$, $\nu_{as}CF_3$). The analyses carried out on the surface of the samples after treatment and then naturally and artificially aged confirmed the presence of the applied silanes. Figure 5 shows the map (11.5 mm ×8.5 mm) obtained on

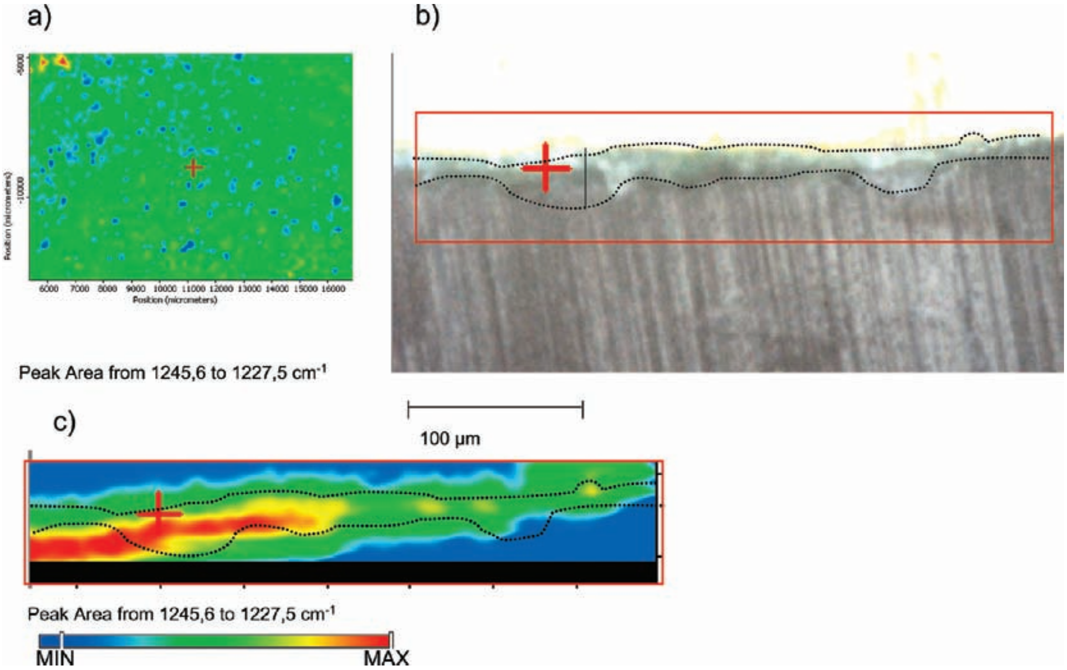

**FIGURE 5.** (a) Superficial mapping in reflection of a MN sample treated with Dynasylan F8263 and exposed in Cabo Raso for 18 months, distribution map of the silane protective (peak area from 1245 to 1227 cm$^{-1}$); (b) FTIR microscope image of the sample cross section; the red box indicates the selected area for the ATR raster scanning; (c) FTIR false color plots representing the distribution map of the silane protective (peak area from 1245.6 to 1227.5 cm$^{-1}$).

one MN sample treated with T1S after natural aging. The mapping with the integrated system allows analysis of larger areas with more statistical information about the total composition of the sample. The high energy output, in fact, allows to reduce the scan numbers (in this case four scans for spectrum), therefore reducing the total time of acquisition without affecting the spectral quality. It is worth noting (Figure 5a) that the silane distribution appears almost homogeneous within the low spatial resolution selected (150 $\mu$m). One fragment of the sample was cut off and embedded in polyester resin in order to evaluate the silane location, which appears to be distributed on the whole patina thickness (Figure 5b and c). Further investigations are being performed to compare the different patina behaviors and to understand how aging may affect the silane content and distribution.

## 7. Conclusions and Future Perspectives

Our research group is currently studying new analytical strategies involving FTIR spectroscopy and microscopy in order to develop analytical methods that can be used for routine analysis. These techniques may in fact be widely employed in museums or restoration laboratories thanks to their ease of use and the limited amount of sample needed.

Considering our initial results, we believe that far-IR spectroscopy, especially in the ATR mode, can be particularly useful for the characterization of mid-IR inactive compounds when applied to mural paintings, metal corrosion, and stone degradation products where a more abundant amount of sample is often available.

The same technique is presently under evaluation as a potential tool for the characterization of organic compounds employed in the conservation field. The first results demonstrate that far infrared spectra provide diagnostic information complementary to that obtained in the mid range. Moreover, our research is devoted to test instrumental tools (such as beam condenser, or integration with optical devices for the sample location on the macro ATR crystal) or specific sample preparation in order to reduce the sample amount. We believe that this technique may be particularly useful for routine analyses because many spectrometers can be uploaded with the far-infrared detector with a limited money expense.

While the possibilities of mid FTIR microscopy and spectroscopy for the identification of inorganic compound are well established, we consider a strategic topic the characterization of organic substances. In particular, we are now working in the frame of the European project CHARISMA for the development of analytical protocols in which FTIR microscopy can be employed together with other techniques with an integrated approach. Particular attention will be devoted to sample preparation in order to avoid the embedding resin contamination and to improve the surface planarity. We are also investigating the diagnostic possibilities offered by the new integrated microscope configuration. So far, this new system has proved to be effective for the characterization of small particles and thin layers. Even if the spatial resolution is not comparable with that obtained with SR light, this system can provide interesting results when it is not possible to access to SR facilities and the layers or particle dimensions are suitable for this technique (10 $\mu$m).

Another important task is the study of protective products performances. In this field, FTIR microscopy can be particularly useful in order to characterize the patina composition affecting the protective performances and to evaluate the treatment distribution and in-depth penetration. In particular, this integrated system allows the mapping of a wide area in order to obtain more statistical information.

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## FOOTNOTES

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